

SURVEY OF INORGANIC POLYMERS

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BY

ARTHUR H. GERBER
EUGENE F. McINERNEY

HORIZONS RESEARCH INCORPORATED

23800 Mercantile Road
Cleveland, Ohio

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16. Abstract A literature search covering the period 1957-1978 was carried out in order to identify inorganic, metallo-organic, and hybrid inorganic-organic polymers that could serve as potential matrix resins for advanced composites. The five most promising candidates were critically reviewed and recommendations made for the achievement of their potential in terms of performance and cost. These generic polymer classes comprise: <div style="margin-left: 40px;"> (1) Poly(arylsilsesquioxanes), (2) Poly(silylarylene-siloxanes), (3) Poly(silarylenes), (4) Poly(silicon-linked ferrocenes), and (5) Poly(organophosphazenes). </div> No single candidate currently possesses the necessary combination of physico-mechanical properties, thermal stability, processability, and favorable economics. The first three classes exhibit the best thermal performance. On the other hand, poly(organophosphazenes), the most extensively studied polymer class, exhibit the best combination of structure-property control, processability, and favorable economics.					
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KEY WORDS

Boron polymers
Carborane polymers
Carborane-siloxane polymers
Carbosilane polymers
Chelate polymers
Composites
Coordination polymers
Ferrocene polymers
Heat resistant polymers (plastics, elastomers)
Inorganic polymers
Matrix polymers
Metallocene polymers
Organometallic (metallo-organic) polymers
Phthalocyanine polymers
Phosphazene polymers
Phosphonitrilic polymers
Poly (organophosphazenes)
Poly (silylenes)
Poly (siloxane-ferrocenes)
Poly (silsesquioxanes)
Poly (silylarylene-siloxanes)
Silylene-siloxane polymers
Silylene polymers
Silicon polymers
Siloxane polymers
Structure-property relationships
Thermally stable polymers (plastics, elastomers)

ABSTRACT

A literature search covering the period 1957-1978 was carried out in order to identify inorganic, metallo-organic, and hybrid inorganic-organic polymers that could serve as potential matrix resins for advanced composites. The five most promising candidates were critically reviewed and recommendations made for the achievement of their potential in terms of performance and cost. These generic polymer classes comprise:

- (1) Poly(arylsilsesquioxanes),
- (2) Poly(silylarylene-siloxanes),
- (3) Poly(silarylenes),
- (4) Poly(silicon-linked ferrocenes), and
- (5) Poly(organophosphazenes).

No single candidate currently possesses the necessary combination of physico-mechanical properties, thermal stability, processability, and favorable economics. The first three classes exhibit the best thermal performance. On the other hand, poly(organophosphazenes), the most extensively studied polymer class, exhibit the best combination of structure-property control, processability, and favorable economics.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
ABSTRACT	iii
1.0 PROGRAM OBJECTIVES	1
2.0 PROGRAM SUMMARY	1
3.0 PROGRAM ORGANIZATION	1
3.1 Literature Survey	
3.1.1 Selection of Systems to be Surveyed ...	2
3.1.2 Generation of Computer and Hand Searches	5
3.2 Critical Review	
3.2.1 Introduction	6
3.2.2 Criteria for Critical Review	7
3.2.3 Discussion of Individual Criteria	9
4.0 INORGANIC POLYMERS LITERATURE SURVEY AND BIBLIOGRAPHY	
4.1 Polymers with Non-Carbon Backbone	
4.1.1 Non-Carbon Side Groups	11
(a) Polysilicates	11
(b) Polyborates	11
(c) Polyphosphates	12
(d) Miscellaneous	12
4.1.2 With Carbon Side Chains	
(a) Siloxanes	13
(b) Siloxanes Containing Non-Metal in Backbone	14
(c) Metallo-Siloxanes	14
(d) Aluminum and Boron Polymers	15
(e) Poly(metal phosphinates) and Poly(phosphonatolanes)	16
(f) Poly(organophosphazenes) and Poly(organophosphazanes)	22

TABLE OF CONTENTS (Contd.)

<u>Section</u>	<u>Page</u>
4.1.3 No Side Groups	27
(a) Silicon Nitride	27
(b) Boron Nitride	28
(c) Polysulfur Nitride	28
4.1.4 Bibliography	29
4.2 Polymers with Carbon and Metal Backbone	
4.2.1 Non-Carbon Side Groups	38
(a) Coordination Polymers	38
(b) Miscellaneous	51
4.2.2 Polymers Containing Carbon & Metal in Backbone with Carbon Side Groups ..	52
(a) Metallocenes	52
(b) Coordination Polymers	63
(c) Organometallic Polymers without Metallocene in Backbone	69
4.2.3 Bibliography	75
4.3 Polymers with Carbon and Non-Metal Backbone	
4.3.1 Non-Carbon Side Groups	84
4.3.2 Carbon Side Groups	94
(a) Poly(carbosilanes)	94
(b) Poly(carbosiloxanes)	95
(c) Poly(carborane-siloxanes)	100
(d) Non-Siloxane Carborane Polymers with Carbon Side Groups	111
(e) Miscellaneous B-, B-N-, B-P-, Ge-, Si-Containing Polymers ...	112
4.3.3 Bibliography	120
5.0 CRITICAL REVIEW CANDIDATES	
5.1 Poly(arylsilsesquioxanes)	
5.1.1 Introduction	127
5.1.2 Method of Preparation	127
5.1.3 Properties	131
5.1.4 Summary and Recommendations	137
5.1.5 Bibliography	139

TABLE OF CONTENTS (Contd.)

<u>Section</u>	<u>Page</u>
5.2 Poly(silylarylene-siloxanes)	143
5.2.1 Introduction	144
5.2.2 Methods of Preparation	144
5.2.3 Properties	150
5.2.4 Summary and Recommendations	161
5.2.5 Bibliography	164
5.3 Poly(silarylenes)	
5.3.1 Introduction	167
5.3.2 Methods of Preparation	167
5.3.3 Physical Properties	169
5.3.4 Summary and Recommendations	170
5.3.5 Bibliography	172
5.4 Poly(silicon linked ferrocenes)	174
5.4.1 Introduction	174
5.4.2 Methods of Preparation	176
5.4.3 Properties	184
5.4.4 Summary and Recommendations	189
5.4.5 Bibliography	195
5.5 Poly(organophosphazenes)	199
5.5.1 Introduction	199
5.5.2 Methods of Preparation	200
5.5.3 Properties	204
5.5.4 Summary and Recommendations	217
5.5.5 Bibliography	220
6.0 BIBLIOGRAPHY	
6.1 General References	225
6.2 Author Bibliography	227
7.0 ACKNOWLEDGEMENTS	298
8.0 DISTRIBUTION LIST	301

LIST OF TABLES

<u>Section/Table</u>	<u>Page</u>
3.0 I Polymers of the Type $\leftarrow M-L \rightarrow_n$	2
4.1 I Properties of Poly(metal phosphinates) ...	18
II Properties of $\rightarrow [Al(X)O-P(O)(R)-O]_n$	20
III Properties of $\rightarrow [Al(OP(O)R^2R^3)O-P(O)R'-O]_n$	21
IV Cyclolinear and Cyclomatrix Poly(organo-phosphazenes)	24
4.2 I Chelate Groups Useful in the Preparation of Metal Coordinated Polymers	40
II Polyferrocenes Containing C, H, N, O, Halogen	54
III Ferrocene Polymers Containing Other Metal or Non-Metal (B, P, S) Atoms	59
IV Non Iron-Containing Metallocene Polymers .	64
4.3.1 I Polymers with Carbon and Non-Metal Atom Backbone and No Carbon Side Groups	88
4.3.2 I Properties of Polyesters of Diphenyl-silicic Acid	97
II Physical Transition Temperatures of Selected Poly(carborane-siloxanes)	106
III Mechanical Properties of Uncured Poly-(carborane-siloxane) as a Function of Molecular Weight	109
IV Mechanical Properties of Modified Carborane-Siloxane Vulcanizate	110
V Carboranyl Polymers Linked by N, P, Ge and Containing Carbon in Side Groups	111
VI Boron-Nitrogen Containing Polymers	114
VII Miscellaneous Polymers with B, P, or Ge in Backbone	119

LIST OF TABLES (Contd.)

<u>Section/Table</u>	<u>Page</u>
5.2 I Effect of Structure of Some Siloxane Modified Poly(silarylenes) upon Tg	152
II Effect of Structure of Some Other Siloxane Modified Poly(silarylenes) upon Tg	155
III Effect of Sequence Length of Silylarylene- Siloxane Block Copolymers upon Physical Properties	158
IV Effect of Increasing p-Silphenylene Content in Block Copolymers upon Physical Properties	159
V Effect of Block Component upon Physical Properties of Poly(TMPS-DMS) Copolymers ..	160
5.4 I Hydrolytic Stability of Poly(ferrocenyl- siloxane) and Poly(silylarylene-siloxane).	185
II Properties of Polymers Prepared by Diol- Diaminosilane Polycondensation	186
III Thermal Parameters of Selected Oxysilane Polymers	187
IV Thermo-oxidative Stability of Poly- [(silanyl-siloxanyl)ferrocene].....	187
V Thermo-oxidative Stability of Some Poly- (silanyl)- and Poly(siloxanyl)-ferrocenes .	188
5.5 I Transition and Decomposition Temperatures for Various Poly(phosphazenes), [R ₂ PN] _n ..	205
II Effect of Heat Aging on PFAP Vulcanizate Properties	208
III Tensile Properties of Poly(fluoroalkoxy- phosphazene) Cast Films	211
IV Tensile Test of Poly[di(p-chlorophenoxy)- phosphazene] films	211

LIST OF TABLES (Contd.)

<u>Section/Table</u>	<u>Page</u>
5.5 V Mechanical Properties of PMR Polyimide and Polyphosphazene-Polyimide/-Glass Laminates	213
VI Isothermal Heat Aging in Air of Poly- (decaboranyl-phosphazenes)	214

LIST OF FIGURES

<u>Section/Figure</u>	<u>Page</u>
4.3 1 Dynamic Thermogravimetric Analysis of Diphenylsilicic Acid	98
2 Effect of Heat Aging on Properties of Poly(decaboranyl-phosphorous linked) Composites	117
5.1 1 Stress Strain Plots for Organosilicon Ladder Polymers at T = 100°C	133
2 Temperature Dependence of Ultimate Elongation of Poly(phenylisobutyl- silsesquioxane)	134
3 Shrinkage Kinetics of Selected Poly- (silsesquioxanes)	135
4 E' vs Temperature Plots of Selected Poly- (silsesquioxanes)	135
5 Tg δ Temperature Plot for Organosilicon Ladder Polymers	136
5.2 1 Thermogravimetric Analysis of Poly- (arylene -siloxanes)	153
5.5 1 Change in Solution Viscosity of PFAP with Time	208
2 Retention of 50% Modulus for Reinforced PFAP Vulcanizates after Aging in Air (200°C)	208
3 Effect of Heat Aging on Flexural Strength of Poly(decaboranyl-phosphazene) Composites	215
4 Effect of Heat Aging on Flexural Modulus of Poly(decaboranyl-phosphazene) Composites	215

SURVEY OF INORGANIC POLYMERS

1.0 PROGRAM OBJECTIVES

The objectives of this program are (1) to survey the technical literature for the purpose of identifying inorganic polymer systems having potential application in preparing advanced fiber-reinforced composites, and (2) to select the five most promising candidates generated from the survey and subject them to critical review.

2.0 PROGRAM SUMMARY

Developments in inorganic polymer technology were examined between 1957 and 1978, making use of both computer as well as hand searching techniques. Three major polymer classifications were identified and investigated leading to the selection of the following five candidate systems:

- (1) Poly(arylsilsesquioxanes)
- (2) Poly(silylarylene-siloxanes)
- (3) Poly(silylarylenes)
- (4) Poly(silicon linked ferrocenes)
- (5) Poly(organophosphazenes)

Communications were conducted with experts in the field.

3.0 PROGRAM ORGANIZATION

The survey was organized and carried out according to the following format.

- Task I - Literature Survey
 - A. Selection of systems to be searched.
 - B. Generation of computer and hand searches.
- Task II - Critical Review
 - A. Establishment of criteria for critical review candidates.
 - B. Selection and critique of five candidate systems.
 - C. Recommendations.

Task III - Preparation of bibliography and
final report.

3.1 Literature Survey

3.1.1 Selection of Systems to be Surveyed

The scope of polymers examined includes linear, cyclic and 3-dimensional species which predominantly contain one or more of the following structural features in the polymer backbone:

- a. Type $\{M-L\}_n$ as shown in Table I.

TABLE I
POLYMERS OF TYPE $\{M-L\}_n$

M	L		
	Oxygen	Nitrogen	Phosphorus
From Group III			
B	X	X	X
Al	X	X	
From Group IV			
Si	X	X	
Sn	X		
Pb	X		
From Group V			
P	X	X	
As	X	X	
Sb	X	X	
From Group VI			
S	X	X	
Transition Metals			
Ti	X	X	
Zr	X	X	

- b. Significant amounts of both C-C and C-M bonds where M is selected from B, Si, Al, Ge, Sn, Pb and Sb.

- c. Polymers having three or more different elements, other than carbon, in the backbone, such as poly(elementosiloxanes) [$\{Si-O-M\}$ where M may be B, Al, Zn, Ti, Zr, or other polyvalent metals, P, S], poly(metal phosphinates).
- d. Coordination (chelate) and metallocene polymers where the metal is an integral component of the backbone. The metallocene may be either homoannularly or heteroannularly incorporated into the main chain.

Certain inorganic polymer systems were excluded from consideration in this study. These include:

- a. $\{M-L\}_n$ polymers where $M = L = Se, Te, Sb, Be$ or As .
- b. Polymers that largely contain C-C, C-N or C-O bonds in the main chain will be considered as organic polymers.
- c. Polymers containing appreciable Ge-O bonds in backbone.
- d. Hetero-chain polymers containing Si-O-P, Si-O-As or Si-O-Sb bonding.

Selenium and tellurium are highly toxic and both homo-chain and hetero-chain polymers of Se and Te do not offer advantages over analogous sulfur polymers. Bond energies of the excluded $\{M-L\}_n$ polymers are usually 50 kcal/mole or less and therefore stable polymers would not be anticipated. Polymers containing Ge-O bonds are generally unstable to acids and bases and depolymerize reversibly to lower molecular weight materials. Polymers containing Si-O-P, Si-O-As, or Si-O-Sb bonds are hydrolytically unstable and chemically unstable to acids and bases.

With these exclusions accounted for, the inorganic polymer classes were then categorized in the following fashion prior to carrying out the literature search.

I - NON-CARBON BACKBONE

- 1. Non-Carbon Side Groups

- (a) Polysilicates (including aluminosilicates and borosilicates)
- (b) Polyborates
- (c) Polyphosphates (including alkali borophosphates, metal doped)
- (d) Miscellaneous

- 2. Carbon Side Groups

- (a) Siloxanes
- (b) Siloxanes containing non-metal in backbone
- (c) Metallo-siloxanes
- (d) Aluminum and boron polymers
- (e) Poly(metal phosphinates) and poly(phosphonates)
- (f) Poly(organophosphazenes) and poly(organo-phosphazanes)

- 3. No Side Groups

- (a) Silicon nitride
- (b) Boron nitride
- (c) Polysulfur nitride

II - CARBON AND METAL IN BACKBONE

- 1. Non-Carbon Side Groups

- (a) Coordination polymers
- (b) Miscellaneous

- 2. Carbon Side Groups

- (a) Metallocenes
- (b) Coordination polymers
- (c) Organometallic polymers without metallocene in backbone

III - CARBON AND NON-METAL BACKBONE

- 1. Non-Carbon Side Groups

- 2. Carbon-Side Groups

- (a) Poly(carbosilanes)
- (b) Poly(carbosiloxanes)
- (c) Poly(carborane-siloxanes)
- (d) Non-siloxane carborane polymers with
carbon side groups
- (e) Miscellaneous B-, B-N-, B-P-, Ge-, Si-
containing polymers

3.1.2 Generation of Computer and Hand Searches

Chemical Abstracts was hand searched from 1967-78 using the following key words:

Coordination compounds
Metallocenes
Organometallic compounds
Phosphonitrile compounds
Phthalocyanine
Polyester, preparation
Polyphosphates, polymers
Plastics manufacture and processing
Polymers, analysis
preparation
properties
siloxanes, ladder
silarylene
silphenyl
silarylene, siloxanes (silphenylene-siloxane)
poly(arylene-siloxarylenes)
poly(arylsilsesquioxanes), poly(phenyl-
silsesquioxanes)
oxysilane polymers
polysiloxanes
silazanes
ferrocenes
uses and miscellaneous
Synthetic high polymers

The period between 1957-1966 was not searched in Chemical Abstracts because of the wealth of texts and review articles published during this interval.

Defense Documentation Center (DDC) computer searches, including current work and the period 1957-1978 coupled with an Ohio State University search (Chemical Abstracts) covering the period 1974-1978 was carried out using the following key words:

- Aluminosilicate/polymers
- Boron-containing polymers
- Carborane/polymers
- Carborane-siloxane polymers
- Chelate polymers
- Coordination polymers
- Cyclosilazanes, cyclosiloxanes/polymers
- Inorganic composites
- Inorganic polymers
- Metal phosphinates/polymers
- Metallocenes/polymers
- Metal (zinc, zirconium) organo polymers
- Organosilane polymers
- Phthalocyanine/polymers
- Phosphonitrile (polyphosphazene) polymers
- Poly(aluminosiloxane)
- Poly(borates)
- Polyesters/metal-containing
- Poly(metal phosphinate)
- Poly(phosphates)
- Poly(silicates)
- Poly(stannoxane)
- Poly(titanoorganosiloxane)
- Siloxanes and silicones
- Structure-property relationships

3.2 Critical Review

3.2.1 Introduction

Before analyzing the major classifications of inorganic polymers, it would be appropriate to provide the reader with a general overview of polymer properties relevant to program objectives.

Two main transitions in polymers are glass transition (T_g) and the crystalline melting point (T_m). T_g is an important basic property of an amorphous polymer because it determines what temperature the material will be an elastomer or hard solid. This in turn determines the use temperature

range. Transition temperatures have been determined by differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and torsional braid analysis (TBA). Many times results are dependent on the time scale of the experiment.

Physico-mechanical properties, before and after exposure to severe environments (heat or chemicals), can usually be greatly improved by crosslinking. Several formulation parameters which affect crosslinking optimization include concentration and type of filler, crosslinking agent, stabilizer, resin-filler interaction, polymer structure, and polymer molecular weight.

Thermo-oxidative stability, deformation under load, hydrolytic stability at elevated temperature are also important properties to consider in the design of fiber reinforced resin composites. A major disadvantage of current reinforced epoxy composites is their loss of performance upon heating in the presence of moisture. Therefore, any readily hydrolyzed polymer would be of questionable value for consideration of high performance reinforced composites.

Several other factors must be considered with regard to preparation of a fiber filled resin composite for high temperature applications. These include proper wetting of resin with fiber, stability of cured resin to fiber, method of prepregging resin to fiber, cure conditions, and polymer plasticization if any. Ideally, one would desire a solvent-free resin that is mobile or readily softened and that can be cured to a thermosetting material at moderate temperature (\geq softening temperature) and pressure. Use of solvents are disadvantageous because inadequate removal creates voids which lower ultimate tensile and flexural moduli.

One sophisticated, efficient method to improve resin processability by plasticization is to use a reactive, nonvolatile, low molecular weight polymer analog. Such an additive enhances processability by lowering the effective softening point and subsequently is incorporated into the polymer structure during the curing or postcuring step.

3.2.2 Criteria for Critical Review

The polymers surveyed in Task I were reviewed to determine viable matrix resin candidates for use in advanced fiber reinforced composites. Candidate polymers were judged on the following criteria, presented in the order of decreasing priority:

- a. Mechanical properties over a range of temperatures.
- b. Thermo-oxidative stability.
- c. Potential for processing at moderate temperatures and pressures.
- d. Potential for low cost synthesis.
- e. Chemical resistance.

Those polymers which fulfilled the requirement imposed by criterion (a) were advanced successively through the remaining criteria. Those systems not eliminated by this process were then subjected to critical analysis in terms of:

- a. Current status of the polymer system.
- b. Range of properties attained to date.
- c. Shortcomings in the chemistry of the system.

Several limitations were encountered in applying these criteria to all systems considered.

Firstly, there is a paucity of physico-mechanical data or even isothermal aging data at elevated temperatures. Secondly, comparisons of thermal stability and thermal decomposition temperatures from one investigator to another may not be valid because of differences in one or more of the following:

- a. Method of instrumental analysis [thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), torsional braid analysis (TBA)].
- b. Test atmosphere (air, nitrogen, argon, vacuo).
- c. Heating rate, and
- d. Exposure time.

TGA was most widely used to determine thermal stability and/or decomposition temperatures. This is often a good guide to determine direction in structure-property relationships but

often bears little resemblance to long term isothermal aging at elevated temperatures. Extreme caution must be exercised with TGA data because significant property changes may occur without noticeable weight loss. A third major limitation in existing literature is that several well characterized polymer systems have been groomed primarily for the development of broad temperature serviceable elastomers as opposed to thermoplastic or thermosetting materials. Therefore, extrapolation of properties to plastic polymeric counterparts may be tenuous. Widely studied polymers which have often been tailored for a combination of low T_g with high thermal stability include poly(siloxanes), poly(arylene siloxanes), poly(carborane-siloxanes), and poly(organophosphazenes).

3.2.3 Discussion of Individual Criteria

a. Mechanical Properties

Desirable candidate polymers should show high tensile strength, some minimal elongation, high flexural strength and modulus, and high retention of mechanical properties after thermal aging in air at elevated temperatures (possibly up to 700°F). Desirable mechanical properties at ambient temperature of unfilled polymer are given below.

Tensile strength, psi	10,000-30,000
Elongation at break, %	3-12
Flexural strength, psi	10,000-30,000
Flexural modulus, psi	100,000-500,000

b. Thermo-oxidative Stability

Potential matrix resin candidates should show good thermo-oxidative stability. Isothermal aging in air at elevated temperatures was considered a more reliable index to stability than thermal gravimetric analysis (TGA) in air. Desirable levels of stability of unfilled resin will be considered as 90% weight retention after 500 hours at 600°F (315°C) in air. Retention of at least 70% of mechanical properties after this aging would probably be a better barometer of thermo-oxidative stability.

c. Cost

Factors that were considered in determining potential cost included availability and cost of starting materials; efficiency (overall percent yield) of the monomer and polymer synthesis; polymerization conditions; and likelihood of more promising methods for the preparation of monomer(s) and/or polymer.

d. Processing

Moderate processing conditions are defined as utilizing temperatures of 400°C or less and pressures of 1000 psi or less. Factors that were considered for determining processability under moderate conditions are polymer solubility, glass transition temperature (T_g), polymer melt or softening temperature, temperature to initiate crosslinking (if any), compatibility with glass and graphite fibers, and ease of injection and compression molding, and extruding.

e. Chemical Resistance

Criteria for judging good chemical resistance are given below:

1. Good stability (i.e. little weight change and high retention of mechanical properties) to water at elevated temperatures.
2. Little or no effect (swelling) to common organic solvents.
3. Little or no effect to oxidizing (e.g. O₂, O₃, Cl₂, N₂O₄, peroxides, HNO₃, and possibly chromic acid, perborates, perchlorates) and reducing agents.
4. Good resistance to acidic and alkaline agents.
5. Stable to light.

4.0 INORGANIC POLYMERS LITERATURE SURVEY AND BIBLIOGRAPHY

4.1 Polymers with Non-Carbon Backbone

4.1.1 Non-Carbon Side Groups

Polymers in this classification have been divided into four groups.

- (a) Polysilicates (including aluminosilicates and borosilicates).
- (b) Polyborates
- (c) Polyphosphates (including alkali borophosphates, metal doped).
- (d) Miscellaneous

(a) Polysilicates

These materials are considered to fall under the designation of glasses and, although they possess exceptional thermal stability and chemical resistivity, they are not readily processable at moderate temperatures and pressures. Thus, although they represent excellent filler candidates, they are excluded from further consideration in this study.

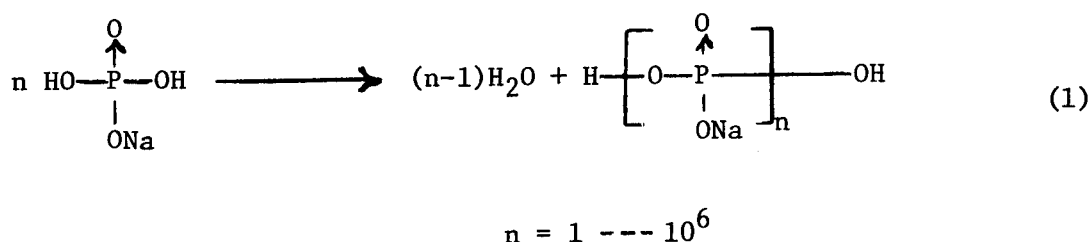
The reader is referred to three excellent reviews of this type [1-3] as well as specific journal citations in the current literature [4-9].

(b) Polyborates

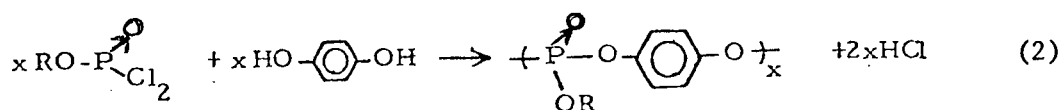
Inorganic polyborates are best treated as a subclass of polysilicates, i.e. borosilicates (see above). Organic polyborates are generally derived from the esterification of boric acid with diols, such as bisphenols, or polyols. However, a major shortcoming of B-O linked polymer is their susceptibility to undergo hydrolysis as well as their tendency to undergo thermal rearrangement. The subject of boron polymers has been extensively reviewed [10-11].

(c) Polyphosphates [12-14]

This class of materials is generally derived from the polycondensation of alkali metal dihydrogen phosphates as shown in Equation (1).



These glass-like, water soluble polymers may be linear, cyclic, or crosslinked in nature. Short chain or cyclic polyphosphates are of enormous importance as detergents. Crosslinked polyphosphates (either through P-O-P or ionic crosslinking via polyvalent cations) are useful as ion exchange resins [15]. Other phosphorus-containing polymers are discussed in Sections 4.1.2, 4.3.2e, and 5.5. It should be noted that certain polyphosphates have been found to possess useful properties. For example, aromatic polyphosphates (the phoryl resins) which are prepared from phosphorodichloridates with aromatic diols (Equation 2), give macromolecules of high transparency, hardness, adhesion and flame retardancy; however, these substances lack long term hydrolytic stability.



For this reason polyphosphates are excluded from further consideration. The reader is referred to a general treatment of polymeric phosphorous compounds for further details [16-17].

(d) Miscellaneous

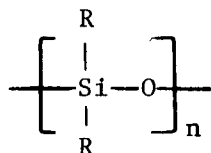
The only materials in this category which merit attention are aminoboranes. Like most other boron polymers

they are quite prone to hydrolysis. Recently, polymeric amino-borane $(H_2BNH_2)_n$ and aminodifluoroborane $(F_2BNH_2)_n$ were prepared and characterized [18]; and, although still hydrolytically unstable, they possess good thermal stability. Boron-nitrogen-containing polymers with carbon side groups are treated in Section 4.3.2e.

4.1.2 With Carbon Side Chains

(a) Siloxanes

Polymers in which silicone-oxygen represent the repeating link in the backbone are generally referred to as silicones and can be best depicted by the general formula



R = alkyl and/or aryl

Designed primarily as insulating fluids/coatings and as elastomers these materials have been the subject of exhaustive investigation since their discovery and have been reviewed in depth (19-26) with more recent advances noted in references [27-32].

A major deficiency associated with silicones, as well as several other inorganic polymer systems (phosphorous-nitrogen, boron-nitrogen) involves the effect of ring-chain equilibria upon both their preparations and their thermal characteristics. Formation of the material is thermodynamically controlled which means that the same (or approximately similar) equilibrium mixture may often be achieved via different routes. Thus, small ring-linear chain equilibria is a major factor in determining both the possibility of preparing polymers from cyclic oligomers and the possibility that polymers will thermally degrade to cyclic oligomers. Steric requirements of substituents bonded to main chain atoms affect this equilibrium. Large bulky groups create more crowding in polymer relative to cyclic oligomers, thereby destabilizing the polymer at elevated temperatures. Thermal reversion or unzipping to cyclic specie can be decreased or prevented by use of smaller substituents, introduction of blocking groups into the backbone, and by changing the electronegativity properties of substituent groups (see also Sections 4.1.2b, 4.3.2b, c, e, 5.1, 5.2, and 5.4.4).

Considerable effort has been spent in improving the thermal stability characteristics of silicones primarily via the use of chain terminating groups directly bonded to silicon (33). Of particular interest is the work which has been done with poly-(diphenylsiloxane) (35-41). Theoretically, this material and/or poly(methylphenylsiloxane) should prove to be an interesting candidate for advanced composites if high molecular weight and good thermal stability can be achieved.

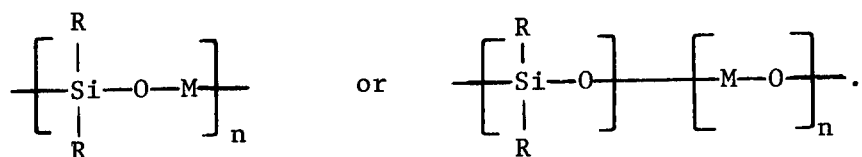
(b) Siloxanes Containing Non-Metal in Backbone

Recently, organosiloxanes containing phosphorous and sulfur in the chain have been reported [42], but most of the work which has been carried out in this area has centered around silicon nitrogen polymers (silazanes).

Silazanes have been the subject of intense interest [43-58] because of the exceptional thermal stability exhibited by these materials. However, the silicon-nitrogen bond is quite sensitive to hydrolysis although silazanes derived from silicon tetrafluoride (e.g. $[\text{SiF}_2\text{N}(\text{CH}_3)_2]$) are claimed to be resistant to alkaline hydrolysis and are stable up to 400°C [59]. Another deficiency associated with silazanes is their strong propensity to form rings rather than long chains during the course of their preparation. Heating of these small ring compounds has been found to yield thermally and hydrolytically stable materials which are infusible and insoluble. Continued heating leads to formation of silicon nitride.

(c) Metallo-Siloxanes [60-62]

Considerable effort has been spent in attempting to enhance the thermal stability of siloxanes via incorporation of metal atoms into the polymer backbone



Elements from Groups III (B, Al); IV [Ge, Sn(+2), Sn(+4), Pb]; V [P, As(+3), As(+4), Sb]; VI (S); as well as transition elements [Ti(+4), V, Cr(+6), Fe(+3), Co, Ni, Zr(+4), Mg, Cu(+2), Zn, Hg(+2)] have been employed but in general the resulting poly(element siloxanes) exhibit thermal and hydrolytic stabilities which are inferior to the parent polysiloxane. As a consequence of the extensive work carried out in this area it is ascertained that

introduction of metal-oxygen linkages results in increased polarization of the bond leading to a higher probability of nucleophilic attack upon the backbone. In spite of these deficiencies activity in this area remains high [63-72] if for no other reason than to gain insights into degradation mechanisms.

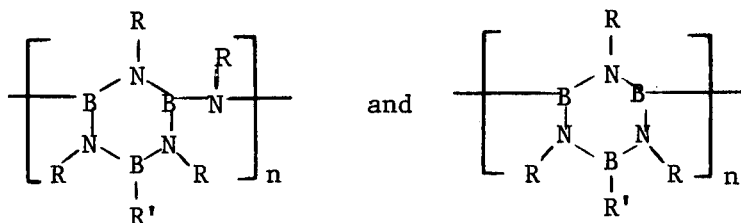
(d) Aluminum and Boron Polymers

Polymers of aluminum containing aluminum-oxygen or aluminum nitrogen linkages in the backbone have been shown to exhibit poor resistance to hydrolysis and have not therefore been the subject of intense interest. Aluminum-oxygen polymers [73] have found use as lubricants, fuel additives, etc. [74-80]. Efforts directed towards improving the hydrolytic stability of these materials have involved the use of coordination complexes [81-83].

Aluminum-nitrogen polymers [84-86], also known as polyalumazanes, have been shown to exhibit good thermal stability up to temperatures as high as 300°C but are sensitive to both moisture and oxygen. Aluminum-phosphorus polymers have also been investigated [86] but these materials are even less stable than the aluminum-nitrogen analogues.

An unusual class of materials incorporating aluminum-fluorine-aluminum linkages was found [87] to be exceptionally stable at high temperatures (400°C).

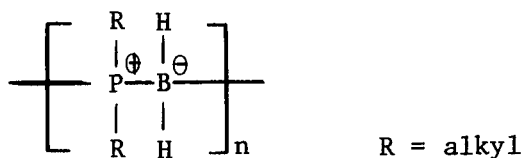
As mentioned in Sections 4.1.1b, c, polymers of boron containing boron-oxygen and boron-nitrogen linkages are very susceptible to hydrolytic attack. The introduction of carbon side groups does result in some improvement in the deficiency by virtue of steric protection and this factor is also responsible for partial suppression of cyclic rearrangement products (also see Section 4.3.2e). In spite of numerous efforts however there has been only marginal success [88,89] in the preparation of useful boron polymers. For example, extensive study has been made of boron-nitrogen polymers derived from borazine [11, 90-92] because of the high thermal stability exhibited by these materials. Polymers of the types



where R and R' = alkyl, aryl

have been prepared [93,94] and show no thermal degradation at temperatures of 400°C. Those polymers which have borazine-carbon linkages in the main chain are discussed in Section 4.3.2e.

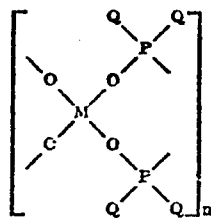
Boron phosphorus polymers have been exhaustively studied by Burg [95-96] and Wagner [97-98]. Phosphino-borane polymers of the type



have been prepared [99] albeit in low molecular weight. A major deficiency with polymers of this class is the tendency to depolymerize to trimeric and tetrameric materials as temperatures above 300°C.

(e) Poly(metal phosphinates) and
Poly(phosphonatolanes)

Poly(metal phosphinates) are a unique class of coordination polymers having the general structure



Q = alkyl or aryl

M = metals having a coordination number of 4 or 6.

This class of materials has been extensively researched by Block and coworkers [100], and has been the subject of several reviews [101-103].

The properties of poly(metal phosphinates) are determined by the coordination metal and ligand (e.g. H₂O), the nature of the

side groups on phosphorus, and the number of bridging sites per center. For example, polymeric beryllium, zinc, and cobalt salts of diphenyl, dimethyl, and phenylmethyl phosphinic acids have been shown to exhibit superior thermal stability up to 500°C with melting points above 200°C [104,105].

Some polymers in the class exhibit molecular weights as high as 150,000; others possess tensile strengths of several thousand psi; still others are soluble in organic solvents, can be cast as films, are fusible, etc. (see Table I). To date, however, no one member of the class has successfully combined any three major properties required by the charter of this study (cf. Section 3.2.2).

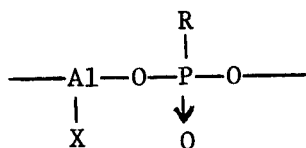
TABLE I

PROPERTIES OF POLY (METAL PHOSPHINATES)^a [103]

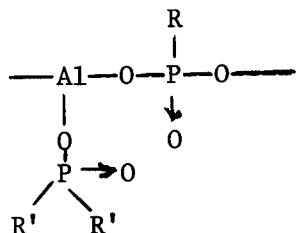
Empirical formula	Solvents	T _m (x)	T _g (A) T _g	T _D ^b	[η] (dl/g)	Ten. str., (psi)	Elongn. (%)
Al[OP(C ₆ H ₅)(C ₇ H ₇)O] ₂ [OP(C ₇ H ₁₃) ₂ O]	(CH ₂) ₄ O	295		400	~35		
Al[OP(C ₆ H ₅)(C ₇ H ₇)O] ₂ [OP(C ₈ H ₁₇) ₂ O] ₂	(CH ₂) ₄ O	315		400	37		
Be[OP(CH ₃) ₂ O] ₂	—	465		542 ^c , 522 ^b			
Be[OP(C ₆ H ₅) ₂ O] ₂	C ₆ H ₆ , CHCl ₃ , CCl ₄	452		515 ^c , 415 ^f			
Be[OP(CH ₃)(C ₆ H ₅)O] ₂	C ₆ H ₆	> 500		525 ^c , 500 ^g			
Be[OP(C ₆ H ₅) ₂ O] ₂	—	> 500		530, 610 ^g			
Be[OP(C ₆ F ₅) ₂ O] ₂	—	> 500		470 ^g			
Co[OP(CH ₃) ₂ O] ₂	H ₂ O	342-343	85	445			
Co[OP(CH ₃) ₂ O] ₂	H ₂ O, C ₆ H ₆ , CHCl ₃	275	130	445			
Co[OP(CH ₃)(C ₆ H ₅)O] ₂ [OP(C ₈ H ₁₇) ₂ O]	—	> 450		485			
Co[OP(C ₆ H ₅) ₂ O] ₂	—	—		336			
Cr(C ₃ H ₇ O ₂)[OP(C ₆ H ₅) ₂ O] ₂	C ₆ H ₆ , CHCl ₃	—	—	> 350 ^d	0.13		
Cr(H ₂ O)(OH)[OP(CH ₃) ₂ O] ₂	H ₂ O, CHCl ₃	—	—	365	0.2-0.3		
Cr(H ₂ O)(OH)[OP(CH ₃)(C ₆ H ₅)O] ₂	CHCl ₃	—	—	375, 355 ^e	0.03-1		
Cr(H ₂ O)(OH)[OP(C ₆ H ₅) ₂ O] ₂	CHCl ₃ , C ₆ H ₆ , O(C ₂ H ₅) ₂ O	—	—	490		> 1900 ^g	
Cr[OP(CH ₃) ₂ O] ₂ [OP(CH ₃)(C ₆ H ₅)O] ₂	—	—	—	—		7000	
Cr[OP(CH ₃)(C ₆ H ₅)O] ₃	—	—	—	—		> 5000	< 1
Cr[OP(C ₈ H ₁₇) ₂ O] ₂ [OP(C ₆ H ₅)(H)O]	—	—	—	420		500	120
Ni[OP(C ₆ H ₅) ₂ O] ₂	—	346		300			
TiCl ₂ [OP(C ₆ H ₅) ₂ O] ₂	C ₆ H ₆ , CHCl ₃	> 300		370	0.03		
Ti[OP(CH ₃) ₂ O] ₂	org. solv.	230-250		450			
Ti[OP(CH ₃)(C ₆ H ₅)O] ₂	C ₆ H ₆ , CHCl ₃	280		435		0.06-0.14	brittle
Ti[OP(C ₆ H ₅) ₂ O] ₂	C ₆ H ₆ , CHCl ₃	300		450		0.06-0.14	brittle
Ti(C ₆ H ₅ O ₂)[OP(CH ₃)(C ₆ H ₅)O] ₂	C ₆ H ₆ , CHCl ₃	> 300		440			
Ti(C ₆ H ₅ O ₂)[OP(C ₆ H ₅) ₂ O] ₂	—	> 300		—			
Ti[OP(C ₆ H ₅) ₂ O] ₄	CHCl ₃ , C ₂ H ₅ OH	135		200			
Zn[OP(CH ₃) ₂ O] ₂	H ₂ O	340		440			
Zn[OP(CH ₃) ₂ O] ₂ [OP(C ₆ H ₅) ₂ O]	C ₆ H ₆ , CHCl ₃	100		430			
Zn[OP(CH ₃)(C ₆ H ₅)O] ₂	C ₆ H ₆ , CHCl ₃	120		425	0.02		
Zn[OP(CH ₃)(C ₆ H ₅)O] ₂ [OP(C ₆ H ₅) ₂ O]	C ₆ H ₆ , CHCl ₃	90	51	430	0.02		
Zn[OP(C ₆ H ₅) ₂ O] ₂	C ₆ H ₆ , CHCl ₃	177, 250	-40	250	0.3-0.7		
Zn[OP(C ₆ H ₅) ₂ O] ₂ [OP(C ₈ H ₁₇) ₂ O]	CHCl ₃	120, 150	-90	—	0.4-0.5		
Zn[OP(C ₈ H ₁₇) ₂ O] ₂	CHCl ₃	dec.		—	0.6		

aT_m(X) is melting point for crystalline form. T₂(A) is softening point for amorphous form. T_D is temp. at which weight loss starts in nitrogen unless otherwise indicated. bTemp. at which weight loss in air is 10%. cTemp. at which weight loss starts in air. dTemp. at which decomposition appears to start in capillary tube. eTemp. at which weight loss in nitrogen is 10%. fTemp. at which weight loss in vacuum is 10%. gSample plasticized with 30% Aroclor 1254.

Closely related to poly(metal phosphinates) are a group of P-O-Al materials known as poly(phosphonatolanes) (I and II).



(I)



(II)

X = halogen
R and R' = alkyl or aryl

Derived from the reaction of etherated aluminum hydride or dialkyl or dialkoxy haloalane with phosphinic acids [106] or phosphinic esters [107] these materials, although initially showing low molecular weight undergo polymer growth in solution (Table II) and exhibit good thermal stability (Tables II and III) [106]. The fluoro(phosphonato)alanes showed unusual resistance to hydrolysis.

TABLE II

PROPERTIES OF POLYMERS OF TYPE $[-Al(X)O-P(O)(R)O-]_n$
 $[m(THF)]_n$ [106]

Polymer No.	R	X	Moles THF per Monomer (m)	Melting Point (°C)	Mol. Wt. (THF) Primary Solution ^a	Mol. Wt. (THF) After Redissolving	Stability TGA (°C) ^b
1	CH ₃	Cl	0.08	Inf. ^c	--	2100 (n = 7.5)	590
2	CH ₃	F	0.10	360-400	Insol.		620
3	C ₆ H ₅	Cl	0.65	Inf.	--	2300 (n = 8.7)	590
4	C ₆ H ₅	F	0.60	440-500	1160 (n = 4.7)	Insol.	695
5	C ₈ H ₁₇	Cl	0.10	Inf.	--	2900 (n = 11)	410
6	C ₈ H ₁₇	F	0.35	340-360	2660 (n = 11)	4700 (n = 18)	420
7	C ₈ H ₁₇ C ₁₂ H ₂₅	F F	0 0.45	340-360 230-280	-- 2100 (n = 6.5)	Insol. ^d 5200-6500 ^d (n = 16-20)	420 380

^a The solvents used for diluting these solutions were obtained by collecting the solvent (on a vacuum line) from a portion of the primary reaction solution.

^b Thermal stabilities were determined by TGA in a nitrogen atmosphere using a heating rate of 10°C/min. The values correspond to the temperature at which the unsolvated polymers began to lose weight.

^c Infusible.

^d Molecular weights of polymers from subsequent reactions were 10,000 (n = 31) and 14,500 (n = 45).

TABLE III

PROPERTIES OF POLYMERS OF TYPE $[-Al(OP(O)R^2R^3)O-P(O)R^1O-]_n$
[106]

Polymer No.	R ²	R ³	R ¹	Melting Point, °C ^a
8	CH ₃	CH ₃	CH ₃	400-430
9	C ₆ H ₅	C ₆ H ₅	CH ₃	450-500
10 ^b	C ₆ H ₅ ^c	CH ₃	C ₈ H ₁₇	350-405
11	C ₆ H ₁₃	C ₆ H ₁₃	C ₈ H ₁₇	320-348
12 ^b	C ₁₂ H ₂₅	C ₁₂ H ₂₅	C ₈ H ₁₇	250-312
13	C ₆ H ₅ CH ₂ ^d	C ₄ H ₉	C ₁₂ H ₂₅	220-235
14	C ₆ H ₅ CH ₂ ^e	C ₇ H ₁₅	C ₁₂ H ₂₅	220-230

^a Melting points were obtained by both a melting point block and by DTA.

^b Polymers X, XI, XII form partially soluble gels in THF.

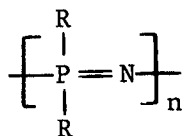
^c Calculated for one THF molecule per monomer unit. The polymer was devolatilized only a short time.

^d The initial molecular weight in THF was 1380 (n = 2.7); after four days the molecular weight increased to 166,000 (n = 340).

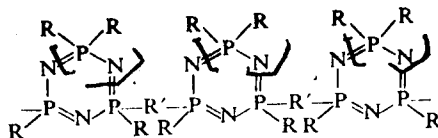
^e The initial molecular weight was 3780 (n = 11.5). After devolatilization and redissolving in THF, the molecular weight increased to 27,000 (n = 83).

(f) Poly(organophosphazenes) and Poly(organophosphazanes)

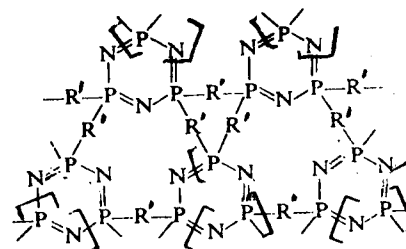
Three structural types of poly(organophosphazenes) have been studied, namely, linear (III), cycloliner (IV) and crosslinked cyclomatrix (V).



(III)



(IV)



(V)

where R = alkyl, aryl, alkoxy, aryloxy,
alkylamino, arylamino

$\text{R}^1 = -\text{O}-\text{R}^2-\text{O}-, -\text{NH}-\text{R}^2-\text{NH}-$

$\text{R}^2 = \text{alkylene, arylene}$

[] for IV and V indicates unit is repeated once or twice

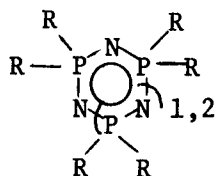
The most widely studied poly(organophosphazenes) (III) are critically reviewed in Section 5.5 and will not be discussed further in this section. Phosphazene polymers (IV) and (V) have been briefly reviewed [108] and in general were produced in low molecular weight or crosslinked, have poor stability, or were not completely characterized.

Cyclotri(and tetra) phosphazenes are rigid structures. To prevent excessive rigidity and insolubility attempts have been made to link these rings with more flexible solubilizing units. Polymerizations have employed several well-known condensation reactions, specifically, transesterification, dehydrochlorination, and nitrogen-elimination (of azides). Representative examples are shown in Table IV.

Cyclomatrix poly(organophosphazenes) (V) are highly rigid, insoluble, high-melting resins produced by cross-linking cyclotri(or tetra)phosphazenes either by polymerization through ethylenic linkages, ligand rearrangement of spiro-phosphazenes, dehydrohalogenation with diols or diamines, or transesterification with polybasic acids (e.g. H_2SO_4 , H_3PO_4 , ArSO_3H , boric acid) or their esters.

Products of good stability resulted when prepolymers derived from chlorophosphazenes and aromatic di- or polyhydroxy compounds are crosslinked with formaldehyde or hexamethylene-tetramine [111,112]. These materials are stable for continuous use at 250°C and for intermittent use up to 540°C . In addition, they possess excellent chemical resistance and have high impact strength.

Cyclomatrix poly(organophosphazenes) (V) are most easily prepared by polymerization of cyclic phosphazenes containing poly(ethylenic) sites as in structure (VI).



R = a) $-\text{OCH}_2\text{CH}=\text{CH}_2$,
b) $-\text{NH}-\text{CH}_2-\text{CH}=\text{CH}_2$

(VI)

Polymerization of (VIb) at $130-220^\circ\text{C}$ in the presence of organic peroxides afforded hard cross-linked resins [113]. Ninety percent of polymer weight is retained to 400°C (TGA) and articles prepared from this resin and glass cloth resist thermal degradation in air above 260°C .

TABLE IV

CYCLOLINEAR AND CYCLOMATRIX POLY(ORGANOPHOSPHAZENES) [108]^a

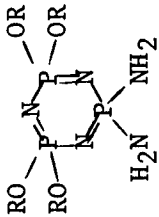
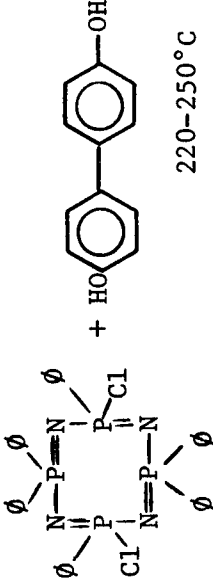
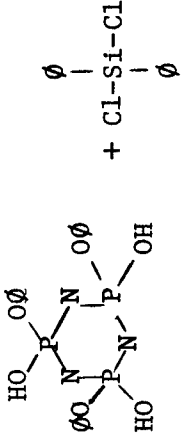
Example	Polymer Derivation	Polymer-Forming Reaction	Remarks
1	 $R = -CH_2CF_3, -CH_2CF_2CF_2H$	Condensation $(NH_3 \uparrow)$	Elastomeric products when $R = C_3H_7F_4$; product insol. and stable in air to 250°C.
2	 $220-250^\circ C$	Dehydrochlorination	M.p. 185-220°C; mol. wt. ca. 500,000; other diols gave lower mol. wts.; thermal dec. >470°C.
3	 $60-160^\circ C$	Dehydrochlorination	Solid polymers; mol. wt. of 6,000; thermal dec. >200°C.

TABLE IV (Contd.)

CYCLOLINEAR AND CYCLOMATRIX POLY (ORGANOPHOSPHAZENES) [108]^a

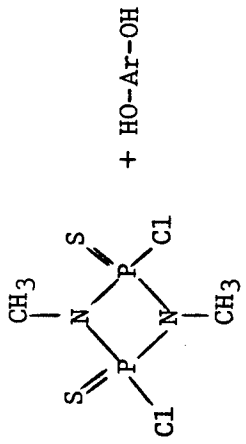

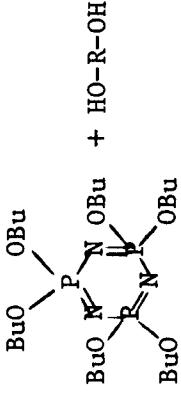
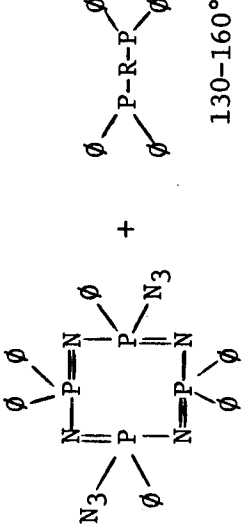

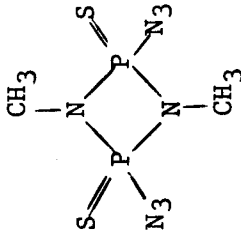

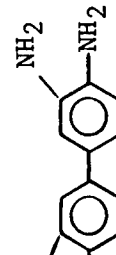
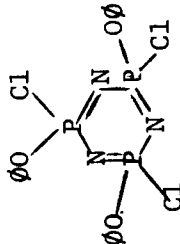
Example	Polymer Derivation	Polymer-Forming Reaction	Remarks
4	 + HO-Ar-OH	Dehydrochlorination	Hard, brittle; stablest when Ar =  m or p; max. T _{dec} = 590°C.
5	 + HO-R-OH	Transesterification (ROH ↑)	Soluble oils or solids; mol. wts. 3,000-10,000.
6	 +  130-160°C	Denitrogenation	Brittle, sol. wts. 9,000-10,000; thermal stability to 400°C.

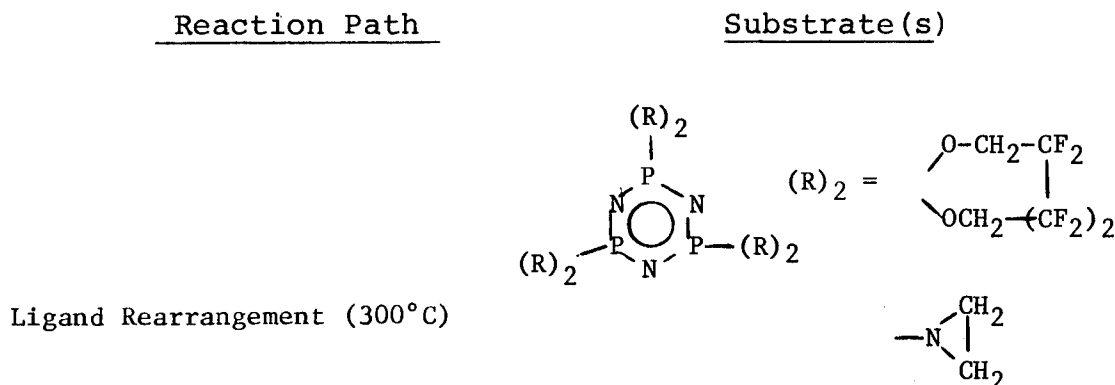
TABLE IV (Contd.)

CYCLOLINEAR AND CYCLOMATRIX POLY(ORGANOPHOSPHAZENES) [108]^a

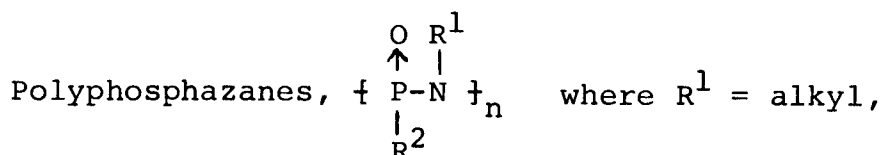
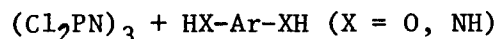
Example	Polymer Derivation	Polymer-Forming Reaction	Remarks
7	  61°C	Denitrogenation	Mol. wts. to 2,600.
8 [109]	 $(\text{Cl}_2\text{PN})_3 + \text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$	Dehydrochlorination	Sl. sol. (polar solvents); poor stability to heat, dil. acids, and alkalis.
9 [110]	 + butyl - and phenyl boric acid	Dehydrochlorination	--

^a And references disclosed therein.

Other means of preparing cyclomatrix polymers (III) are shown below:



Dehydrochlorination polycondensation



phenyl and $\text{R}^2 = \text{phenyl}$, were prepared by self-condensation of phosphonic diamides, $\text{R}-\text{P}(\text{O})(\text{NHR}^1)_2$ [113a]. The polymers were obtained in very low molecular weight (≤ 3000) and were hydrolytically unstable.

4.1.3 No Side Groups

The polymers discussed in this section have no utility as building composites and are therefore treated only peripherally. Because they are considered to be well established materials, only recent references are cited.

(a) Silicon Nitride [114-118]

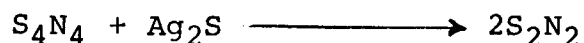
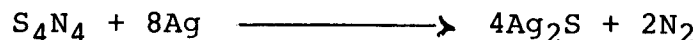
Of the various nitrides of silicon reported in the literature (e.g. SiN , Si_2N_3 , and Si_6N_2) only one, Si_3N_4 , is stable and has industrial importance. It is a fully crosslinked, network polymer obtained by subjecting silane and ammonia to an electrical discharge. Silicon nitride is stable up to temperatures of 1900°C and is used as a refractory and as an abrasive.

(b) Boron Nitride [119-122]

This material (BN) is prepared by heating borax ($\text{Na}_2\text{B}_4\text{O}_7$) in the presence of ammonium chloride at 1000°C . It occurs in two structural modifications; hexagonal (used as an insulator) and tetrahedral (used as an abrasive). It is stable at temperatures up to 3000°C in oxidizing environments.

(c) Polysulfur Nitride [123-129]

Considerable attention has been focused upon this material because of its unusual electrical properties as a superconductor. Its application as a composite material is excluded on the basis of hydrolytic, thermal, and oxidative instability and cost of synthesis. Polysulfur nitride is prepared via the room temperature polymerization of disulfur dinitride (S_2N_2) followed by mild (75°C) heating. The highly explosive S_2N_2 is in turn prepared via the following reaction sequence.



It should be noted that tetrasulfur tetranitride (prepared by the reaction of ammonia and disulfur dichloride) is itself both shock and temperature sensitive.

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4.2 Polymers with Carbon and Metal Backbone

4.2.1 Non-Carbon Side Groups

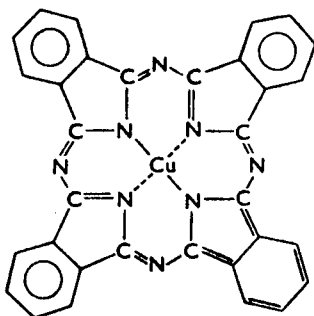
(a) Coordination Polymers (Classes II-1 and II-2-b)

A coordination polymer will be defined as a polymer in which a metal is coordinated with organic ligand(s) to form a polymer containing a metal atom or ion for each monomer unit. A simple structural representation will not be given because of the extreme complexity and numerous possible polymer types. To diminish any further confusion, both polymer Classes II-1 and II-2-b will be included in this section. Numerous chelate ligands and/or polymer structures will be cited.

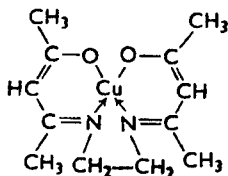
General and specific information on coordination polymers appears in several general references [1-3]. The book by Cotter and Matzner [1] provides excellent coverage on this subject.

Coordination compounds can be prepared by several methods, namely (a) preformed metal complexes may be polymerized through a functional group, (b) a polymer containing a chelate group in the repeating unit can be treated with a suitable metal salt (such as the acetate or acetylacetonate), and (c) polymer formation via reaction of metal-donor atom coordination.

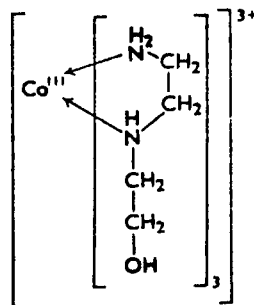
Attempts to prepare stable tractable metal coordinated polymers which might simulate the outstanding thermal and/or chemical stability of model coordinated materials, such as copper phthalocyanine (I), copper ethylenediaminobis-acetylacetonate (II) [4], and cobalt tris(N-hydroxyethyl-ethylenediamine) (III) [5] have been dismal failures.



(I)



(II)



(III)

Copper phthalocyanine is reported to be stable at 500°C, sublimable in vacuo at 580°C, and to resist molten potash and boiling hydrochloric acid [6]. Subsequent work showed (I) was unchanged after 1 hour at 800°C in vacuo [7, 8].

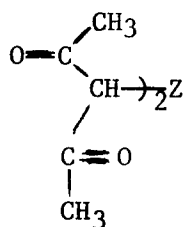
Major problems are largely attributable to one or more of the following: very low molecular weights (generally $\leq 10,000$), insolubility and intractability. Low molecular weights are often due to premature precipitation of product. Further compounding the problem is discouraging thermal stability, except in a few exceptional cases.

A great variety of chelate or metal coordinating groups have been employed in attempts to prepare thermally stable polymers. Usually bis(chelate)-type compounds are employed. Most of these are listed in Table I.

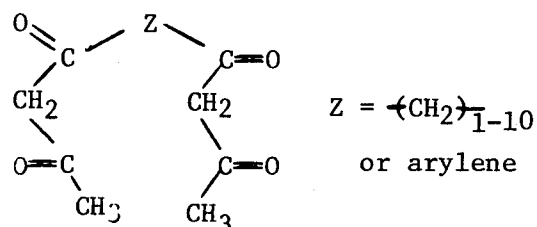
Only a representative number of examples of the many chelate types of polymer-forming materials will be discussed. This will suffice to illustrate the better materials prepared to date, their limitations, and to provide some insight into the possible structural variations.

1. Polymers from Bis(β -diketones)

The poly[metal bis(β -diketonates)] have by far been most widely studied than other polymer chelate systems. Most β -diketones are of two structural types.



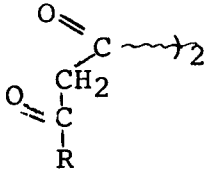
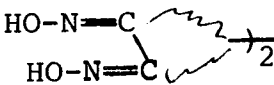
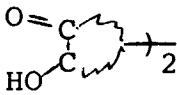
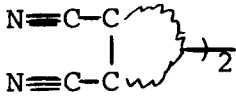
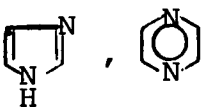
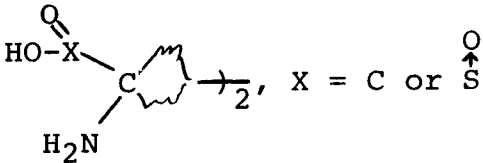
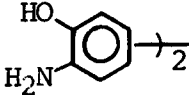
(IV)



(V)

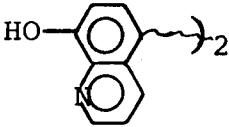
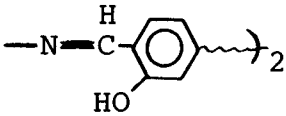
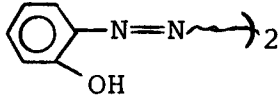
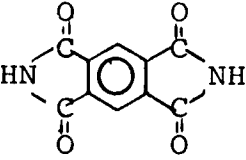
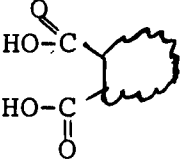
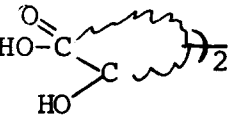
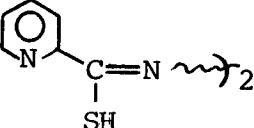
Bulk polymerization of bis(β -diketones) with metal acetylacetonates or metal acetates has been a common procedure for preparing polymers [27, 28, 29]. Basic beryllium acetate was often employed for preparation of beryllium-containing polymers.

TABLE I
CHELATE GROUPS USEFUL IN THE PREPARATION OF METAL
COORDINATED POLYMERS

Chelate Function	General or Specific Representation	Refs.*
1. bis(β -diketones)		
2. bis(1,2-dioximes)		
3. bis(1,2-hydroxyketo)		9, 10
4. bis(o-nitriles or 1,2-dinitriles)		11, 12
5. bis(diamines) (generally heteroaromatic)		13, 14 15, 16,
6. bis(1,2-amino acids)		17
7. bis(o-aminophenols)		

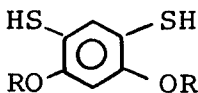
*Pertinent references not cited elsewhere in this section.

TABLE I (Contd.)

Chelate Function	General or Specific Representation	Refs.*
8. bis(hydroxy nitrogen heteroaromatic)		9, 18, 19
9. bis(o-hydroxy Schiff bases)		20, 21
10. bis(o-hydroxyazo)		22
11. bis(imides)		
12. Metal carboxylates	 (with and without adjacent -CO ₂ H or -CNH group)	23, 24
13. bis(α-hydroxyacids)		22, 23
14. bis(thiopicolinamides)		

*Pertinent references not cited elsewhere in this section.

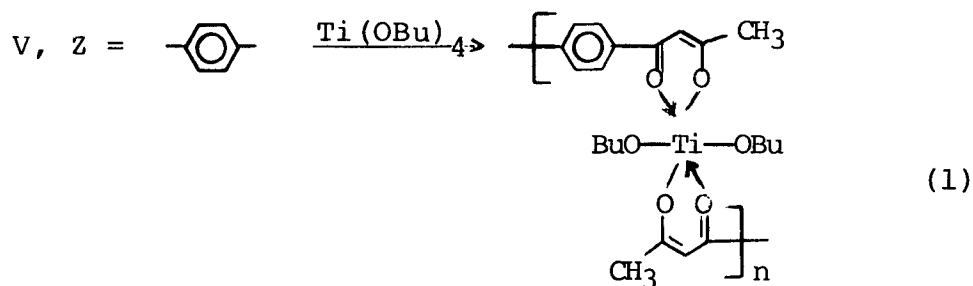
TABLE I (Contd.)

Chelate Function	General or Specific Representation	Refs.*
15. bis(thiooxamides)	$\begin{array}{c} \text{S} \quad \text{S} \\ \parallel \quad \parallel \\ -\text{N}-\text{C}-\text{C}-\text{N}- \\ \text{H} \quad \quad \text{H} \end{array}$	
16. bis(thiosemicarbazones)	$\text{H}_2\text{N}-\overset{\text{S}}{\overset{\parallel}{\text{C}}}-\underset{\text{H}}{\text{N}}-\text{N}=\text{C} \rightsquigarrow_2$	25, 26
17. bis(dithiocarbamates)	$\text{HS}-\overset{\text{S}}{\overset{\parallel}{\text{C}}}-\underset{\text{H}}{\text{N}} \rightsquigarrow_2$	
18. bis(xanthates)	$\text{HS}-\overset{\text{S}}{\overset{\parallel}{\text{C}}}-\text{O} \rightsquigarrow_2$	
19. mercaptide	$\text{R}-\text{SH}$	
20. dimercaptan		
21. cyclophosphazenes with chelating ligands	$\begin{array}{c} \text{X} \quad \text{R} \\ \quad \\ \text{R}-\text{P}-\text{N}=\text{P}-\text{X} \\ \diagup \quad \diagdown \\ \text{N} \quad \text{P}=\text{N} \\ \quad \\ \text{R} \quad \text{X} \end{array} \quad n=1, 2$ <p> $\text{R} = \emptyset, \text{X} = \text{NH}_2;$ $\text{R} = \text{X} = \text{-NHCNH}_2$ </p>	

*Pertinent references not cited elsewhere in this section.

Soluble, very high molecular weight (126,000) polymers were produced from Be^{+2} and 4,4'-di(acetoacetyl)diphenyl ether (V) where $\text{Z} = \text{---}\text{C}_6\text{H}_4\text{---O---C}_6\text{H}_4\text{---}$ [29]. Soluble high molecular weight polymers (intrinsic viscosities to 2.7) were also obtained with Be^{+2} and (V) where $\text{Z} = \text{---}(\text{CH}_2)_6\text{---}$ [30]. In this case a cyclic volatile monomer (or dimer) was obtained by heating an intermediate derivative. The cyclic material was thermally polymerized by maintaining the temperature near the melting point (110°-140°C). These polymers were flexible at room temperature, had high tensile moduli, and strengths. For example, (V) for $\text{Z} = \text{---}(\text{CH}_2)_8\text{---}$, the amorphous polymer had a T_g of 35°C, tensile modulus (25°C) of 122,000 psi, tensile strength of 2710 psi and melt index (190°C) of 0.1-2.0 dg/min. Polymers with aromatic Z radicals (particularly p-disubstituted) tended to be crystalline. Unfortunately, these beryllium poly(chelates) had little practical utility because they gradually reequilibrate to monomer and dimer at temperatures near their formation. Polymers prepared from 3-substituted bis-(β -diketone)-beryllium complexes showed instability above 200°C [31].

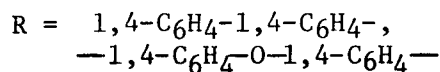
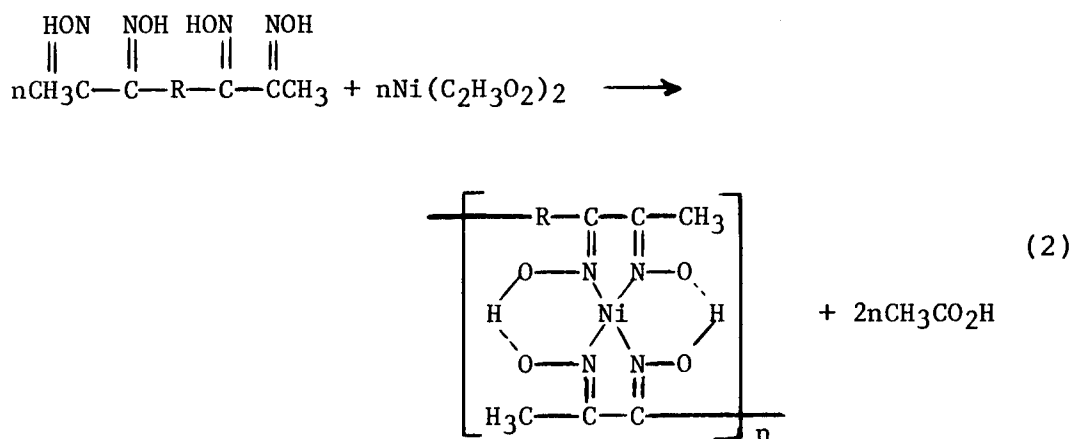
Hexa-coordinating metal atoms can be incorporated into bis(β -diketone) polymers by exchanging a tetraalkoxy titanate with a bis(ligand) [32], as shown in Equation (1). Molecular weights were very low (≤ 2000).



Melting points of metal bis(β -diketonate) polymers are related to their thermal stability. TGA (argon) study of polymers derived from tetraacetylene showed the following decreasing heat stability [33, 34]: $\text{Mg} > \text{Ni} > \text{Co} > \text{Cu} > \text{Zn} > \text{Cd}$. In all cases, including model chelate materials, decomposition occurs in the range 225° to 350°C.

2. Polymers from Bis(1,2-dioximes)

Reaction, Equation (2), of nickel acetate with bis(1,2-dioximes) in methanol gave high yields of polymer. Some pyridine soluble fractions had molecular weights of 20,000 and showed T_m of $>360^\circ\text{C}$ [35, 36, 37].



4. Polymers from Bis(o-nitriles or 1,2-dinitriles)

Much of the earlier work on polymeric phthalocyanines has been reviewed [38].

Tetracyanoethylene (TCNE) forms metal-containing polymers by heating in bulk or with solvents up to 300°C , with metals, metal salts, or metal chelates [39, 40, 41]. Black infusible products result. The copper derivative was partly crystalline, soluble in concentrated H_2SO_4 , and showed a reduced viscosity of 0.8. Copolymers can be prepared by substitution of some TCNE by phthalonitrile.

Heating pyromellitonitrile or 3,3',4,4'-tetracyanodiphenyl ether and phthalonitrile with CuCl_2 also afforded polymers [42, 43].

Another modification of the polymerization involves the generation of tetranitrile component in situ by heating a bis(1,2-dicarboxylic acid) (or corresponding dianhydride) in the presence of a nitrogen source such as urea. Polymeric metal phthalocyanines can be prepared by heating such a mixture with a metal or metal derivative. Low molecular weight products result [44].

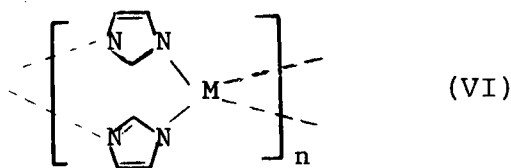
Poly(metal phthalocyanines) were generally reported to decompose in the 250-450°C range in air or in vacuo. One of the more stable such polymers was derived from 3,3',4,4'-tetracarboxybenzophenone which showed a weight decrease at 450°C (TGA) [45].

Polymers have also been prepared from phthalocyanine sandwich intermediates wherein the backbone alternates oxygen with a metal (e.g. Ti) [46] or a non-metal (e.g. Si) [47] and the phthalocyanine is independently bonded to the metal or non-metal.

Non-metal containing phthalocyanine sandwich polymers are discussed in Sections 4.3.1 and 4.3.2e.

5. Polymers from Bis(diamines)

Bis(imidazolato) metal polymers (VI)



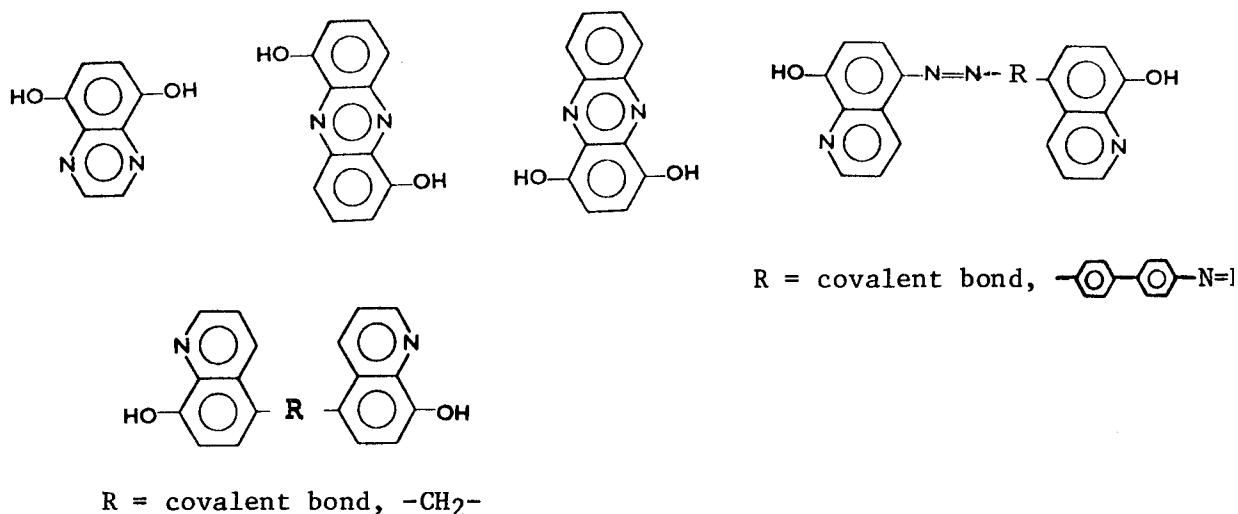
derived from imidazole and metal salts possessed high stabilities where M was Co^{+2} or Zn^{+2} . Weight loss was detectable at 500-575°C in N_2 [48, 49]. These materials were intractable and insoluble. Pyrazine, $\text{N} \equiv \text{N}$, also reacts with metal salts to produce polymers [50].

6. Polymers from Bis(amino acids)

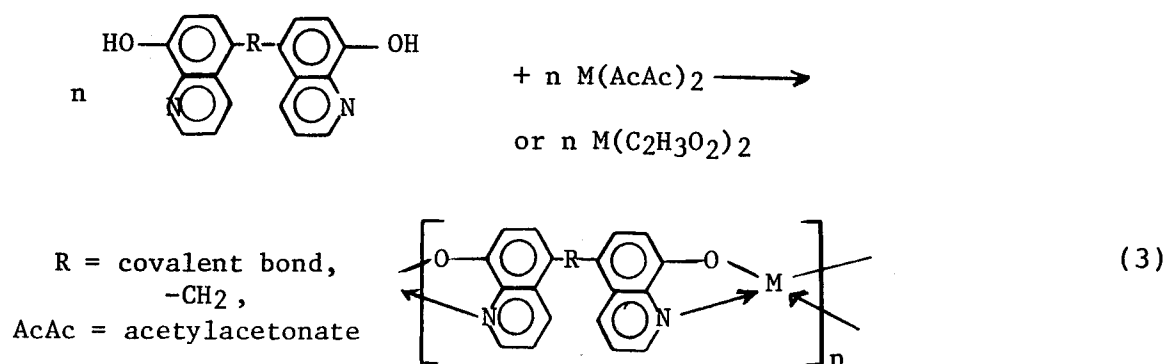
One stimulus to work in this area was the fact that Co^{+3} amino acid complexes exhibit excellent thermal and chemical resistance. However, high molecular weight polymers were not reported [51, 52] from either a bis(o-amino-sulfonic)-biphenyl or α, α' -diaminosebacic acid.

8. Polymers from Bis(hydroxy nitrogen heteroaromatics)

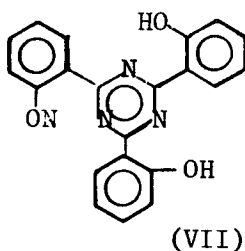
8-Hydroxyquinoline is an excellent complexing ligand for many metal ions. Bifunctional ligands with this structural arrangement are shown below.



Polymerization of bis(8-hydroxy-5-quinolyl) derivatives with a variety of metal sources, even in hot highly polar solvents (refluxing dimethylformamide), usually leads to early precipitation of low molecular weight or infusible products [53, 54, 55].



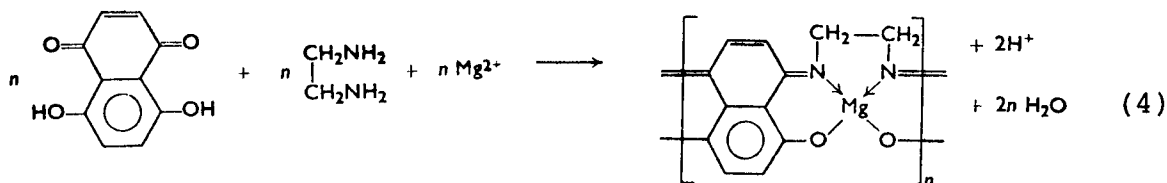
Tris (o-hydroxyphenyl) triazine, (VII),



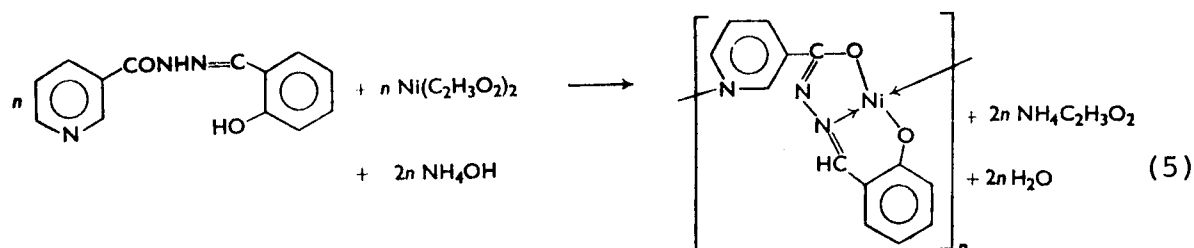
has also been used to prepare polymers [54, 56]. One patent describes the preparation of products from this monomer and boric acid which are thermally stable to 440°C [57]. Thermal stability (TGA, vacuo) of poly(metal 8-hydroxy-5-quinolyl derivatives) are as follows Mn>Ni>Cu<Zn [53, 58, 59]. Decomposition temperatures varied from 350° to 500°C in these studies.

9. Polymers from Bis(o-hydroxy Schiff bases)

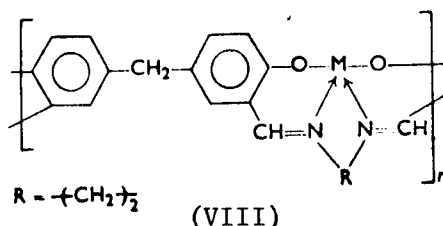
The most direct route (Equation 4 for example) for polymerization of a dicarbonyl compound, a diamine, and a metal salt, led to insoluble products of low molecular weight [60, 61].



A polymer prepared from a nicotinic acid derivative was reported stable to 350°C and resistant to hot alkali [62] (Eq. 5).



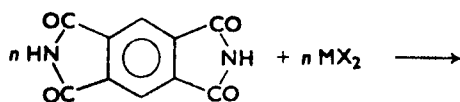
The poly[copper+2.bis(Schiff base)] (VIII) was insoluble and had a reported molecular weight of 76,400 [63, 64, 65].



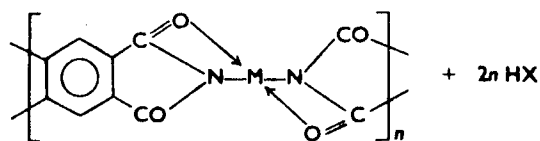
Although monomeric analogs such as the Cu, Ni, and Co complexes of acetylaceton-ethylenediamine may be heated "almost to redness" without decomposition [51], this class of chelate polymers generally decompose in the range 250-350°C [63, 66].

11. Polymers from Miscellaneous Bis(N:O) Ligands

Chelation of pyromellitimide with metals gave polymers reported to be stable in boiling water and stable to 300°C in air after 3 hours [67], (Eq.6). The mercuric chelate decomposed at 510°C in air.

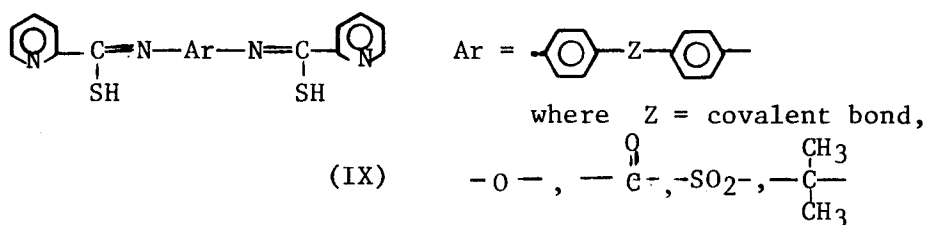


(6)



Amine complexes of divalent metal tetracarboxylic diimide polymers have also been prepared [68, 69]. Thermal stability of the complexes decreased in the order $\text{Zn} > \text{Cd} > \text{Ni} > \text{Cu} > \text{Co}$. Molecular weight of one material was >2000 . The complexes showed crystalline x-ray patterns and were insoluble in conventional solvents.

14. Polymers from Bis(thiopicolinamides)

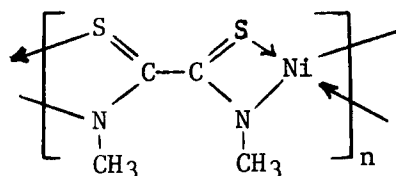


Of the many coordination polymers investigated by J. C. Bailar, Jr. and his co-workers, the poly[metal bis(thiopicolinamides)] showed the best stability. A number of stable poly[metal bis(thiopicolinamides)] were prepared by heating divalent metal acetylacetonates or metal acetates with bis(thiopicolinamides) (IX) [70]. Molecular weights were roughly estimated to be about 15,000. The Zn^{+2} derivative showed the best thermal stability (via TGA). The zinc-containing polymer from (IX) for $\text{Z} = -\text{SO}_2$ did not melt below 300°C and could be heated 6 hours each at 300° and 360°C without appreciable loss in weight or change in infrared spectra. The Zn derivative from (IX), $\text{Z} = \text{covalent bond}$, was found to be stable at 400°C in the absence of air. Marvel et al [71] prepared poly[metal-bis(salicylaldehydes)] and also found the Zn^{+2} derivative to be more thermally stable. A possible reason offered [70] for

the superior stability of Zn^{+2} derivatives is that Zn^{+2} possesses only one oxidation state. Transition metals can be oxidized to higher states and this may catalyze thermal decomposition.

15. Polymers from Bis(thiooxamides)

The Ni^{+2} derivative (X) was crystalline,

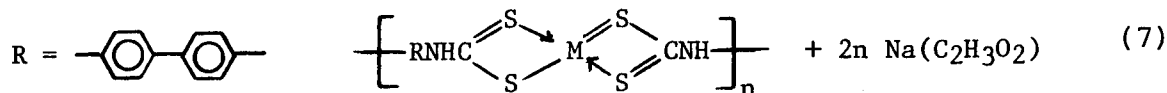
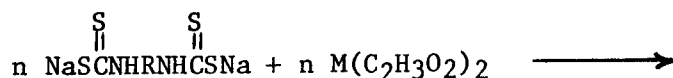


(X)

slightly soluble in hot solvents, and showed a T_m of $>400^\circ\text{C}$ [72].

17. Polymers from Bis(dithiocarbamates)

High molecular weight poly[metal bis(dithiocarbamates)], estimated at 60,000, obtained from Ni^{+2} and Zn^{+2} derivatives were prepared from the disodium salt of bis(dithiocarbamic acids) and appropriate metal acetates, (Eq. 7).



The products were infusible. No mechanical properties were reported [73]. TGA on other similar polymers showed the Ni^{+2} derivative to be stablest [74]. Stability is enhanced when R = aryl but even then appreciable decomposition began at $200^\circ\text{--}300^\circ\text{C}$ in air or inert atmosphere.

21. Polymers from Cyclophosphazenes with Chelating Ligands

Metal-containing polymers derived from the cyclic phosphazene $[(\emptyset)(\text{NH}_2)\text{PN}]_4$ (trans) showed thermal stabilities up to 450°C [75]. Copper salts were most readily incorporated into a polymer network, the most stable polymer was derived from CuSO_4 . Replacement of phenyl by CH_3 or NH_2 or replacement of NH_2 by $-\text{NHCH}_3$ or $-\text{OC}_2\text{H}_5$ decreased stability to below 400°C .

Chelating polymers were prepared from hexakis-(thiocarbamate)cyclotriphosphazene, $[(\text{NH}_2\text{CNH})_2\text{PN}]_3$, using Cu, Ni, and Co ions [76]. The Cu polymer was stablest at 500°C retaining about 80% of its weight (TGA, air).

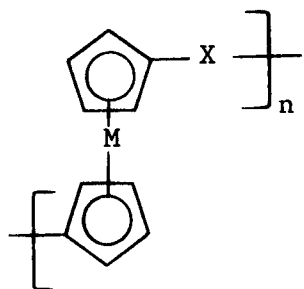
(b) Miscellaneous

One member in this class is poly(carboranyl mercury, $-\{\text{CB}_{10}\text{H}_{10}\text{C}-\text{Hg}\}_n-$. This polymer was prepared from dilithiocarborane and HgCl_2 at 30°C , did not melt to 300°C , and had a molecular weight of 10,000 [77].

4.2.2 Polymers Containing Carbon & Metal in Backbone with Carbon Side Groups

(a) Metallocenes

Most metallocene polymers can be represented by structural formula (XI) or (XII).

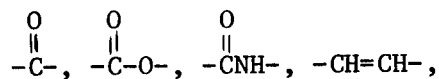


(XI)

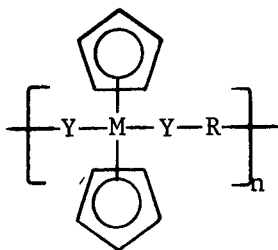
Where $M = \text{Fe}, \text{Co}^{\oplus}, \text{Ru}, \text{Ni}$

X = covalent bond, divalent organic, inorganic or organic-inorganic groups, and combinations thereof.

Typical organic groups include alkylene, alkyleneoxy, arylene, heteroarylene,



$-\text{CH}=\text{N}-$; X may contain non-metal (Si, B, P, Sb) or metal- (Sn, Ti, Zr, Hf, Hg) containing groups.

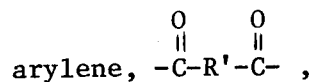


(XII)

Where $M = \text{Ti}, \text{Zr}, \text{Hf}$

Y = covalent bond, O, S, NH

R = covalent bond, alkylene,



where $R' = \text{arylene, metallocene.}$

A considerable number of publications exist on polymers derived from π -cyclopentadienyl (transition metal) complexes. The overwhelming majority of these reports deals with ferrocene-based polymers. Excellent reviews on metallocene chemistry [78,79] and ferrocene polymers [80-83] have appeared since 1967. With the exception of some poly(silicon linked ferrocenes), which are critically reviewed in Section 5.4, metallocene polymers have been found deficient in three respects. First, failure to achieve high molecular weights. Polymers generally have molecular weights of $\leq 10,000$. Second, inadequate thermal stability. Metallocene polymers are not superior to analogous aromatics or heteroaromatics and thermo-oxidative and protolytic stability is poorer. Third, they are not easily amenable to processing. Many ferrocene-containing polymers have shown high conductivity and ultraviolet resistance.

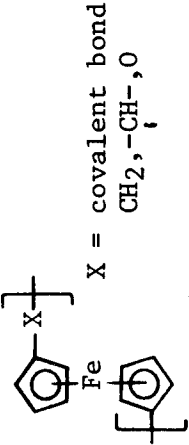
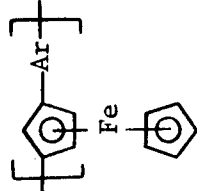
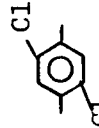
For the most part, synthetic pathways posed to date have not resolved the tendency to form cyclic heterobridged systems and the tendency to give cleavage side reactions which afford branched and crosslinked structures. Polymerization processes employing electrophilic or free radical catalysts are prone to complications because of the polyfunctional behavior of commonly used metallocene substrates. Representative ferrocene-containing polymers and their precursors are shown in Tables II and III.

Ferrocene-containing polyamides, polyhydrazides, polyurethanes, and polyesters have been prepared [78,79,84] from difunctional ferrocenes such as 1,1-dicarbomethoxyferrocene, 1,1'-di(chlorocarbonyl) ferrocene, and 1,1'-bis (α -hydroxyalkyl)-ferrocenes by reaction with glycols, diamines, hydrazines and diisocyanates. These polymers are not obtained in very high molecular weights and offer no thermal or processing advantages over conventional nonferrocene condensation polymers. Modified poly(ethylene terephthalate) containing 1,1'-ferrocene dicarboxylic acid units gave fibers which had improved UV light resistance in comparison to the unmodified polyester [85]. Diepoxide derivatives of ferrocene were copolymerized with phthalic anhydride and *o*-dimethylolcarborane, with phthalic acid and bisphenol A, and with *m*- and *p*-carboranedicarboxylic acids [86]. The resultant polymers were not particularly stable and lost 4 wt. % at 300°C (TGA, air or inert atm.).

Several ferrocene containing polymers have been used in the preparation of composites. Ferrocene copolymerized with terephthaldehyde and 1,1'-ferrocene dicarboxaldehyde gave thermosetting polymers which were suitable for fabrication of glass fiber reinforced structural composites [87a,b]. The laminates contained 23-36% resin, were cured at 400-600°F (204-315°C) and 1000-4000 psi, and gave flexural strengths and moduli of 29,000-33,000 psi and 3 million psi, respectively.

TABLE II

POLYFERROCENES CONTAINING C, H, N, O, HALOGEN [78,79] (a)

Example	Polymer Derivation (b)	Polymer Structure (b)	Remarks
1	1,1'-diacetylferrocene, ZnCl_2 , 180°C	--	Highly crosslinked.
2	Ferrocene, $(t\text{-BuO})_2$, ca. 200°C	 <p>X = covalent bond $\text{CH}_2\text{-CH-},0$</p>	Largely crosslinked + low mol. wt.; m.p.'s < $250^\circ\text{-}300^\circ\text{C}$.
3	Ferrocene + aromatic, $(t\text{-BuO})_2$, $175^\circ\text{-}200^\circ\text{C}$	 <p>Ar = , naphthyl</p>	Mostly insoluble; solubles very low mol. wt.
4	1,1'-dilithioferrocene, CoCl_2 or 1,1'-dilithioferrocene, CoCl_2 , 1,1'-dibromoferrocene	-(Fc)-_n	Low mol. wt.

(a) And references disclosed therein.

(b) Fc = 1,1'-ferrocenylene

TABLE II (Contd.)

POLYFERROCENES CONTAINING C, H, N, O, HALOGEN [78,79] (a)

Example	Polymer Derivation (b)	Polymer Structure (b)	Remarks
5	Ferrocene + $\text{fFc-Hg}\frac{1}{2}$, 245-265°C	$\text{fFc}\frac{1}{2}\text{n}$	Soluble, low mol. wt.; good thermal stability, relative wt. loss of 2, 15, and 25% at 400°, 600°, and 800°C, respectively (TGA, argon).
6	1,1'-Dilithioferrocene + Fc , or $\text{Fc}-\text{Fc}-\text{Fc}$, 0°C	$\text{fFc}-\text{Fc}\frac{1}{2}\text{n}$	Sol. and insol. products; m.p. $\geq 200^\circ\text{C}$ from Fc ; From $\text{Fc}-\text{Fc}-\text{Fc}$ m.p. $>300^\circ\text{C}$, high thermal stability and radiation resistance.
7	Hydroxymethylferrocene, acidic catalyst	$\text{fFc-CH}_2\frac{1}{2}\text{n}$	Mol. wts., to 15,000 (fractionated). Random 1,2-, 1,3-, and 1,1'-disubstitution.
8	<u>N,N</u> -dimethylaminomethylferrocene, $\text{ZnCl}_2 + \text{HCl}$, 150-180°C	$\text{fFc-CH}_2\frac{1}{2}\text{n}$	Sol., mol. wts. to 8,000.
9	Hydroxyalkylferrocene, dilute HCl (H_2O -ethanol)	$\begin{array}{c} \text{R} \quad \text{R} \\ \quad \\ \text{fFc-CH-O-CH}\frac{1}{2}\text{n} \end{array}$ <p style="text-align: center;">R = H, CH_3</p>	Very low mol. wts.; heating with acids led to O-free crosslinked resins.

(a) And references disclosed therein.

(b) Fc = 1,1'-ferrocenylene

POLYFERROCENES CONTAINING C, H, N, O, HALOGEN [78,79] (a)

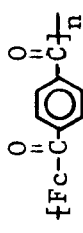

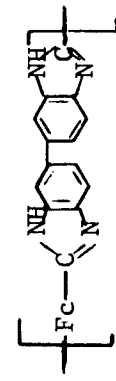
Example	Polymer Derivation (b)	Polymer Structure (b)	Remarks
10	$\begin{array}{c} \text{H} \\ \\ \text{Ferrocene} + \text{RC}=\text{O} \\ 85^{\circ}\text{--}170^{\circ}\text{C, Lewis acid (ZnCl}_2\text{)} \end{array}$	$\begin{array}{c} \text{R} \\ \\ \text{--Fc--CH--} \\ \\ \text{--} \end{array}_n$ <p>R = alkyl, phenyl, substd. phenyl, 2-furyl</p>	Competitive side reactions, low mol. wt., fusible below 200°--250°C.
11	α,ω -Dibromoalkane + sodium cyclopentadienide, then Na and FeCl ₂	$\text{--Fc--(CH}_2\text{)}_x\text{--} \text{--}_n$	Low mol. wt.
12	1,1'-Ferrocene dicarboxaldehyde + 1,4-dicyanobut-2-ene	$\begin{array}{c} \text{--Fc--CH=C--CH=CH--C=CH--} \\ \qquad \qquad \\ \text{CN} \qquad \qquad \text{CN} \end{array} \text{--}_n$	Insol., dec. pt. >230°C.
13	1,1'-Ferrocene dicarboxaldehyde + (Ø) ₃ P(CH ₂) ₂ -C ₆ H ₄ -CH ₂ P(Ø) ₃ + base	$\text{--Fc--CH=CH--} \text{--} \text{C}_6\text{H}_4 \text{--CH=CH--} \text{--}_n$	Sol., m.p. <100°; very low mol. wt.
14	ϵ -Ferrocenylcaproic acid, polyphosphoric acid, $\leq 56^{\circ}\text{C}$	$\begin{array}{c} \text{O} \\ \\ \text{--Fc--(CH}_2\text{)}_5\text{--C--} \\ \\ \text{--} \end{array}_n$	Very low mol. wt., dec. >200°C.
15	Ferrocene + 1,1'-di(chlorocarbonyl)- ferrocene, BF ₃ , 25-75°C, or use of mono(chlorocarbonyl)ferrocene alone	$\begin{array}{c} \text{O} \\ \\ \text{--Fc--C--} \\ \\ \text{--} \end{array}_n$	Sol. and insol. products; relative wt. losses 15-20 and 25-30% at 450° and 500°C, resp. (TGA, argon).

(a) And references disclosed therein.

(b) Fc = 1,1'-ferrocenylene.

TABLE II (Contd.)

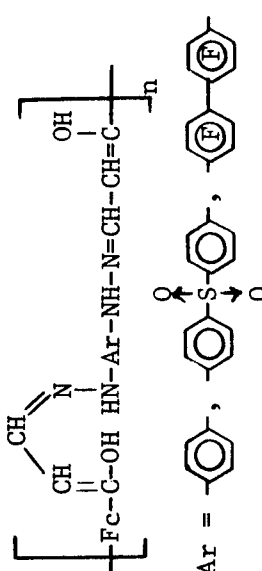
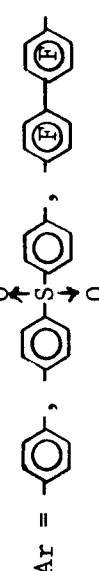
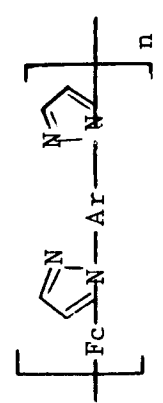

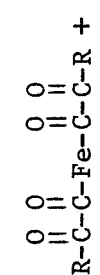
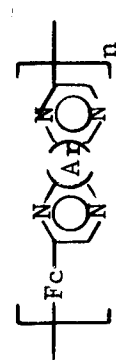
POLYFERROCENES CONTAINING C, H, N, O, HALOGEN [78,79] (a)

Example	Polymer Derivation (b)	Polymer Structure (b)	Remarks
16	Ferrocene + terephthaloyl chloride, ZnCl_2 , $\leq 80^\circ\text{C}$	 $\text{tFc}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{C}_n$	Sol. (mol. wt. ≤ 4700) and insol. products; 1,1'-structure predominant; thermal stability poorer than Ex. 15.
17	Ferrocene + bis(diazotized benzidine)	 $\text{tFc}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_n$	Sol. and insol. products; sol. products very low mol. wt., m.p. $< 120^\circ\text{C}$; high mol. wt. fraction showed exc. stability, wt. loss of 8% at 700°C (TGA, argon).
18	1,1'-Ferrocene dicarboxaldehyde + <i>m</i> - or <i>p</i> -aromatic diamine	$\text{tFc}-\text{CH}=\text{N}-\text{Ar}-\text{N}=\text{CH}-\text{C}_n$	Sol., low mol. wt.
19	1,1'-Dicarbophenoxyferrocene + 3,3'-diaminobenzidine, $210-250^\circ$, then $280-290^\circ\text{C}$	 <p>Polybenzimidazole</p>	Infusible, sol. in HCO_2H ; poor thermal stability; very inferior to arylene analog (i.e., Fc replaced by <i>m</i> - or <i>p</i> -phenylene).

(a) And references disclosed therein.

(b) Fc = 1,1'-ferrocenylene.

TABLE II (Contd.)
POLYFERROCENES CONTAINING C, H, N, O, HALOGEN [78,79] (a)

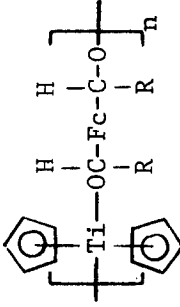
Example	Polymer Derivation (b)	Polymer Structure (b)	Remarks
20	 <p>Ar = </p>		Sol. in H ₂ SO ₄ , insolubility after long heating at 260-300°C; superior thermal stability to Ex. 19; relative wt. loss for Ar =  was 2% and 20% at 400°C and 600°C, resp. (TGA, argon).
21 [88]	1,1'-divinylferrocene, Lewis acids + alkyl Al catalyst (cationic cyclopolymerization favored by increased dissociation of growing ion pair)	--	Extensive crosslinking in molten polymer at ca. 200°C.
22 [89]	 <p>Aromatic bis(o-diamine), 20-200°C</p>		--

(a) And references disclosed therein.

(b) Fc = 1,1'-ferrocenylene

TABLE III

FERROCENE POLYMERS CONTAINING OTHER METAL OR
NON-METAL (B, P, S) ATOMS [78,79] (a)

Example	Polymer Derivation (b)	Polymer Structure (b)	Remarks
1	1,1'-Di(chloromercuri)ferrocene + complexing or reducing agent (e.g., Na ₂ S ₂ O ₃ , NaI)	[Fc-Hg]_n	Very poor solubility; dec. near 300°C.
2	1,1'-Dilithioferrocene + (R) ₂ ZCl ₂ , 0°C	$\begin{array}{c} \text{R} \\ \\ \text{[Fc-Z]}_n \\ \\ \text{R} \end{array}$ Z = Si, Sn R = CH ₃ , ϕ	Mol. wts. 1750-7000; for Z = Si, R = ϕ stability to 350° (TGA, N ₂)
3 [90]	Dicyclopentadienyl titanium dichloride + HOCH-Fc-CHOH $\begin{array}{c} \text{R} \\ \\ \text{HOCH-Fc-CHOH} \end{array}$ + NaOH or (C ₂ H ₅) ₃ N	 R = H, CH ₃	Very poor stability; dec. <200°C.
4 [91]	S ₂ Cl ₂ with ferrocenyl phenol, (α -hydroxyethyl)ferrocene, or bis(α -hydroxyethyl)ferrocene		Ferrocene rings + SS units. Stable in air to 200°C.

(a) And references disclosed therein.

(b) Fc = 1,1'-ferrocenylene.

TABLE III (Contd.)

FERROCENE POLYMERS CONTAINING OTHER METAL OR NON-METAL (B, P, S) ATOMS [78,79] (a)

Example	Polymer Derivation (b)	Polymer Structure (b)	Remarks
5	Ferrocene + $\phi\text{-Z}\begin{array}{l} \text{Cl} \\ \text{Cl} \end{array}$ ZnCl ₂ , 80-170°	$\begin{array}{c} \text{fFc-Zf} \\ \\ \phi \end{array}_n$ $\begin{array}{c} \text{O} \\ \uparrow \\ \text{Z} = \text{P}, \text{P} \text{ (from Z=P after} \\ \text{H}_2\text{O, O}_2, \text{H}_2\text{O}_2), \text{P} \\ \downarrow \\ \text{S} \end{array}$	Cleavage of cyclopentadiene rings at $\geq 140^\circ\text{C}$; low mol. wt., fair thermal stability.
6	1,1'-Dilithioferrocene + 2 ϕBCl_2 , then H ₂ O	$\begin{array}{c} \text{fFc-B-O-Bf} \\ \quad \\ \phi \quad \phi \end{array}_n$	Low mol. wt.; softening 100°-130°C; incipient wt. loss near 350°C (TGA, He).
7	Tetrabutyl 1,1'-ferrocene diboronate + 3,3'-diaminobenzidine, as in Table II, Ex. 22	$\left[\text{Fc} - \text{B} \begin{array}{c} \text{NH}^+ \\ \text{NH}^- \end{array} \text{C}_6\text{H}_4 \begin{array}{c} \text{NH}^+ \\ \text{NH}^- \end{array} \text{B} \right]_n$ Polybenzoborimidazoline (c)	Poor thermal stability, decomposed extensively at 300°-400°C (TGA).

(a) And references disclosed therein.

(b) Fc = 1,1'-ferrocenylene.

(c) Replacement of Fe by  (m or p) gave polymer which melted >550°C and showed good thermal stability to 500°-600°C [92].

TABLE III (Contd.)

FERROCENE POLYMERS CONTAINING OTHER METAL OR
NON-METAL (B, P, S) ATOMS [78,79] (a)

Example	Polymer Derivation (b)	Polymer Structure (b)	Remarks
8 [93]	$R^1\text{-Fc-R}^2 + \text{S}_2\text{Cl}_2$ $R^1 = \text{P-C}_6\text{H}_4\text{NH}_2,$ $\quad \text{-C(CH}_3\text{):NOH;}$ $R^2 = \text{H, -C(CH}_3\text{):NOH}$	Ferrocene polymers with NHSS or :NOSS bridges.	Stable to 200°C in air, dec. temp. 360-420°C.
9 [94]	$\begin{array}{c} \text{R} \quad \text{R} \\ \quad \\ \text{HO-N=C-Fc-C=N-OH,} \\ (\text{Cp})_2\text{TiCl}_2, \text{ base} \end{array}$ $\text{Cp} = \text{cyclopentadienyl}$ $\text{R} = \text{CH}_3, \emptyset$	$\left[\begin{array}{c} \text{Cp} \\ \\ \text{O-N=C-Fc-C=N-O-Ti} \\ \quad \quad \\ \text{R} \quad \text{R} \quad \text{Cp} \end{array} \right]_n$	Sol., low mol. wt., degrades at ca. 250°C; retains 50% wt. to 600°C.

(a) And references disclosed therein.

(b) Fc = 1,1'-ferrocenylene.

Incorporation of 10-20% 1,1'-bis (hydroxymethyl)-ferrocene into a phenolic matrix had little effect on mechanical properties of the resin but increased the char yield by 17% [95]. This suggests potential of the ferrocene modified matrix for use as an ablative, such as in heat shields.

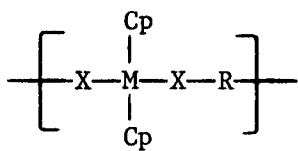
Metallocenes containing metals other than iron have been prepared and are shown in Table IV.


Interest in ruthenocene is based on its greater thermodynamic stability compared to ferrocene [96]. However, the high cost of ruthenium and the reduced nucleophilicity of ruthenocene relative to ferrocene, necessitating more vigorous reaction conditions, have led to very modest efforts of study.

Cobalticinium salts, isoelectronic with ferrocenium derivatives, possess high thermal stability and increased resistance to strong acids or bases or to oxidation [97]. Cobalticinium is appreciably more stable oxidatively than ferrocene, and polymers containing it are expected to show high thermo-oxidative (and probably radiation) stability, being quite superior in this respect to the ferrocene analogs [98]. These observations have led to investigation of the cobalticinium structure in polyesters and polyamides [99-101] (See Table IV, Exs. 9-11). The hexafluorophosphate counterion is strongly preferred because high yields of polymers can be obtained. Other anions such as Br^- , Cl^- , and NO_2^- gave poor yields.

Two serious problems remain to be resolved with polymers containing cobalticinium in the main chain. First, preparation of polymers free from connecting ligands which prevent optimization of thermooxidative stability. Second, the high ionic content of such polymers may eventually afford very thermally stable polymers but at the expense of solubility and processability.

Carraher and coworkers have studied many organometallic condensation polymers (also see Section 4.2.2c), some of which contain metallocene units. Results of thermal analysis were reported [103] for metallocene polymers (XIII) as well as for other organometallic polymers (XIV; Section 4.2.2c). The data indicated that:

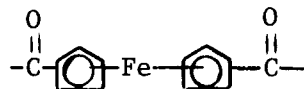
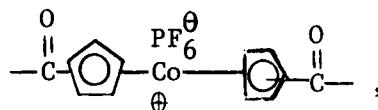
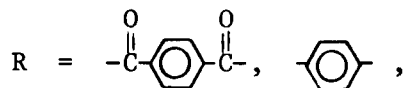


Where Cp = 

M = Ti, Zr, Hf

X = O, NH

(XIII)



- (1) Degradation @ 300 to 500°C in air is usually identical to that in N₂.
- (2) Many Group IVA materials often lose a metal-containing fragment below 500°C whereas Group IVB, cobalticenium, uranyl, and some Group VA containing polymers retain the metal.
- (3) Ferrocene containing polymers lose the ferrocene moiety at 200-300°C.
- (4) Most polymers exhibit medium to poor weight retention at 300-500°C.
- (5) Oxidation usually begins at ≤250°C.

(b) Coordination Polymers

Coordination polymers with carbon side groups have been included in Section 4.2.1a.

TABLE IV

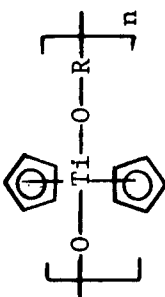
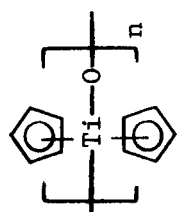
NON IRON-CONTAINING METALLOCENE POLYMERS [78,79] (a)

Example	Polymer Derivation	Polymer Structure	Remarks
1	Ruthenocene + $\text{H}_2\text{C}(\text{OCH}_3)_2$, ZnCl_2		Very low mol. wt.; thermally superior to Fe analog, relative wt. losses of 10, 20, 35% at 450°, 500°, and 600°C, resp. (TGA, argon).
2	Ruthenocene + RCHO , Lewis acid, 140°-195°C R = CH_3 , ϕ , substituted ϕ		Low mol. wt.
3	$\text{NaC}_5\text{H}_4(\text{CH}_2)_4\text{C}_5\text{H}_4\text{Na}$ + NiBr_2		Sol. and insol. fractions; oxidation-sensitive.

(a) And references disclosed therein.

TABLE IV (Contd.)

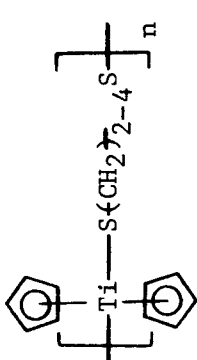
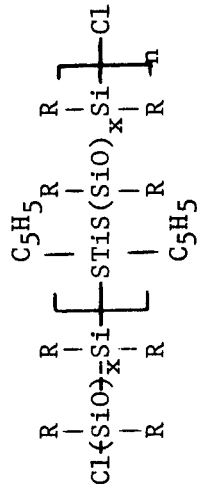
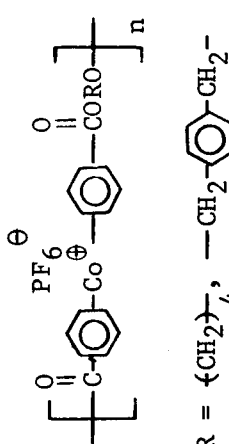
NON IRON-CONTAINING METALLOCENE POLYMERS [78,79] (a)

Example	Polymer Derivation	Polymer Structure	Remarks
4	Titanocene dichloride + alkali salts of diphenols or dibasic acids	 $\left[\text{O}-\text{Ti}(\text{Cp})_2-\text{O}-\text{R} \right]_n$ $\text{R} = \text{C}_6\text{H}_4-\text{S}(\text{C}_6\text{H}_4)_2-\text{C}_6\text{H}_4, \quad \text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{C}_6\text{H}_4$	Very low mol. wt.; high melting.
5	Titanocene di(trifluoroacetate) + dialkoxysilanes	$\text{As above but R} = \begin{array}{c} \text{R}' \\ \\ -\text{Si}- \\ \\ \text{R}' \end{array}$	--
6	Titanocene dichloride, solvent, Zn	 $\left[\text{Ti}(\text{Cp})_2-\text{O}-\text{Z} \right]_n$	Very unstable, eliminates C ₅ H ₆ to give

Z = cyclopentadienyl or polymer chain; poor hydrolytic stability.

(a) And references disclosed therein.

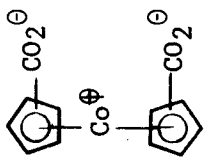
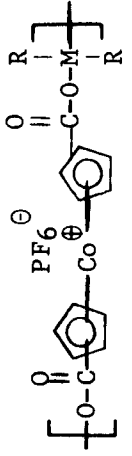
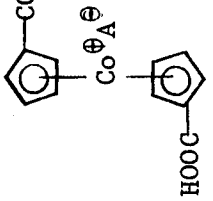
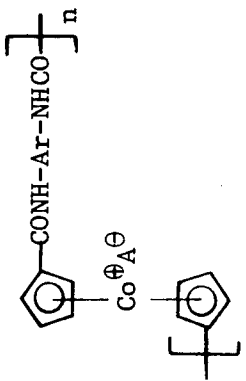
TABLE IV (Contd.)
NON IRON-CONTAINING METALLOCENE POLYMERS [78,79] (a)

Example	Polymer Derivation	Polymer Structure	Remarks
7	Titanocene dichloride, alkane α,ω -dithiol, $(C_2H_5)_3N$		Light and air sensitive, fair thermal stability, limited solubility.
8 [102]	$(C_5H_5)_2Ti(SH)_2$, $(C_2H_5)_3N$, $ClSi(R)_2O[Si(R)_2O]_xSi(R)_2Cl$ $R = CH_3$		$\geq 50\%$ cyclic oligomers, linears low mol. wt. ($n = 6-8$); S-Si bond hydro- lytically unstable.
9 [99]	Cobalticinium 1,1'-dicarbonyl chloride hexafluorophosphate + diol	 <p>$R = -(CH_2)_4-$, $-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-$</p>	Sol. and insolubles; low mol. wt.

(a) And references disclosed therein.

TABLE IV (Contd.)

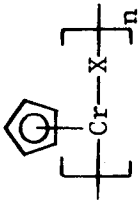
NON IRON-CONTAINING METALLOCENE POLYMERS [78,79] (a)

Example	Polymer Derivation	Polymer Structure	Remarks
10 [99]	 $+R_2MCl_2$	 $R = \text{alkyl, phenyl}$ $M = \text{Sn, Ti, Zr, } \emptyset\text{Sb-}$	Poor solubility; mol. wt. 2,000-80,000; all degraded to cobalticgenium 1,1'-di-carboxylic acid by prolonged contact with salt solutions.
11 [100]	 $+ H_2N-Ar-NH_2$ $+ SbCl_3,$ $150-175^\circ C$	 $A = PF_6, SbCl_4$ $Ar = \begin{matrix} p-C_6H_4 & p-C_6H_4 \\ & \\ p-C_6H_4-CH_2 & p-C_6H_4 \end{matrix}$	Soluble and film-forming; mol. wt. estimated at 3,000-6,000 [98]; TGA not performed.

(a) And references disclosed therein.

TABLE IV (Contd.)

NON IRON-CONTAINING METALLOCENE POLYMERS [78,79] (a)

Example	Polymer Derivation	Polymer Structure	Remarks
12	Chromocene + sulfur or selenium	 $\left[\text{Cp}-\text{Cr}-\text{X} \right]_n$ <p>X = S, Se</p>	Poor solubility.

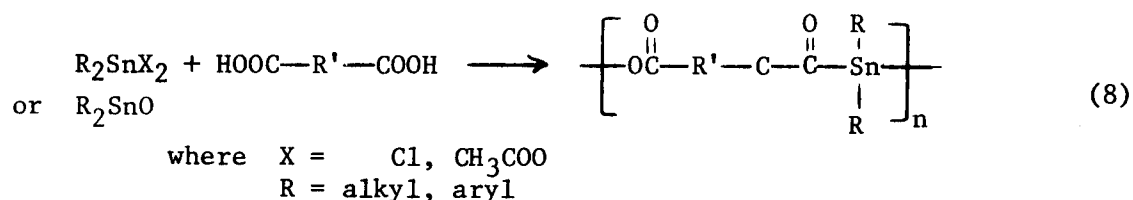
(a) And references disclosed therein.

(c) Organometallic Polymers Without Metallocene in Backbone

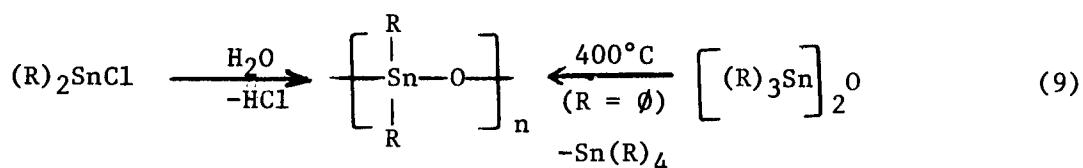
The polymers in this section are too diverse to be represented by a simple structural formula.

For the most part the polymers discussed in this section display many of the deficiencies shown by the coordination polymers in Section 4.2.2a, namely, low molecular weight, poor solubility and processability, and poor to moderate thermal stability. These polymers have been prepared by condensation processes which have utilized esterification, displacement, and hydride addition reactions. Much of the earlier work in this area dealt with the preparation of tin-containing polymers.

One of the simplest methods for introduction of metal atoms into a polymer backbone consists in esterifying a metal compound containing two displaceable groups with a dicarboxylic acid (or salt) as shown in Equation (8) [104].



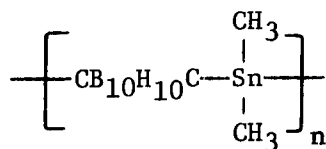
Other tin-containing polymers, poly(dialkyl-diaryltin oxides), were prepared from different organo tin compounds as shown in Equation (9) [105].



The polydialkyltin and polydiphenyltin oxides are crystalline, brittle, insoluble in polar solvents, high melting substances (285-400°C) which decompose at or slightly above their melting points.

Reaction of dibutyltin dibutoxide and dibutyltin diacetate gave benzene soluble, linear, low molecular weight (ca. 4,200) polymers with melting points of 96-100°C. The melt could be drawn into fibers and showed good glass adhesive properties [106].

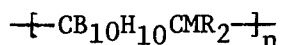
Metallorganic polymers (XIV) containing carborane



(XIV)

units were prepared by reaction of $(\text{CH}_3)_2\text{SnCl}_2$ and/or $(\text{CH}_3)_2\text{GeCl}_2$ with dialkali metal derivatives of *m*- and/or *p*-carborane at 0°C [107]. Molecular weights were low (≤ 2000 to 9000). The meta carborane polymers were more soluble and lower melting (ca. 220-250°C) than their para analogs (m.p. 365 to >400°C). A composite with good thermal stability was prepared from the *m*-carborane polymer and spinning grade chrysotile asbestos. The composite exhibited its original tensile strength (1200 psi) after 100 hours air exposure at 800°F (427°C).

Similarly, metal and non-metal containing *m*-carboranes of structure (XV)



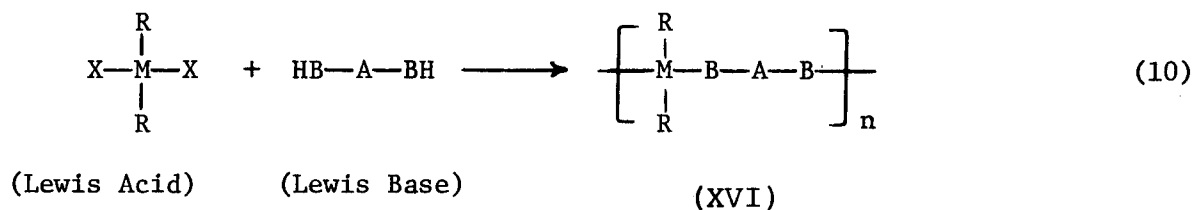
M = Si, Ge, Sn, Pb
R = CH₃, Ø

(XV)

were prepared from dilithio *m*-carborane and R_2MCl_2 [108]. The polymers ranged in melting points from 65 to 250°C and in molecular weights (\bar{M}_n) from 450 to 9500.

Carraher and coworkers have extensively studied linear organometallic polymers represented by the general formula (XVI)*.

* A number of these polymers contain non-metal atoms, e.g., Si, Ge, As, Sb, and are discussed in Section 4.3.2e.



Where R = cyclopentadienyl, lower alkyl, phenyl

M = Sn, Pb, Pt, MoO₂, Ti, Zr, Hf,
UO₂, Si, Ge, As, Sb, Bi

B = O, NH

A = nil, alkylene, arylene

Most of this work has been summarized recently [103, 109-111], particularly with respect to polymerization procedures, solubility parameters, and thermal analysis. A number of polymers contained cyclopentadienyl-metal units wherein the metal was titanium, zirconium, hafnium, or cobalticinium (also see Section 4.2.2a). Successfully employed monomer intermediates for the chemistry in Equation (10) are shown below in Table V.

TABLE V

COMPONENTS FOR THE PREPARATION OF CONDENSATION POLYMERS
CONTAINING METAL, GROUP IVA, OR GROUP VA ATOMS [109b]

Lewis Bases

Dihydrazines	Diols
Hydrazines	Dithiols
Ureas	Diacids
Thioureas	Diamidoximes
Diamines	Dioximes
Dihydrazides	

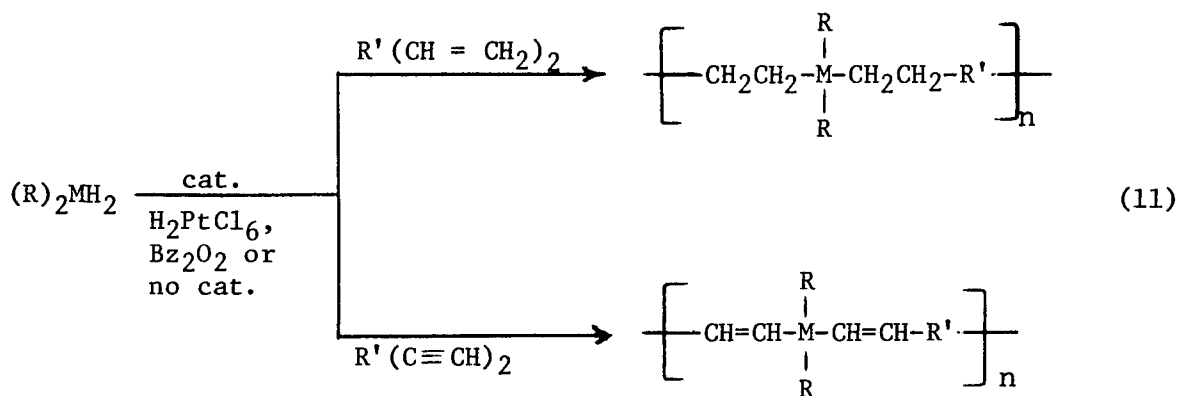
Lewis Acids

R ₂ SiX ₂	R ₂ PtX ₂	MoO ₂ Cl ₂
R ₂ GeX ₂	R ₂ AsX ₂	R ₂ TiX ₂
R ₂ SnX ₂	R ₃ SbX ₂	R ₂ ZrX ₂
R ₂ PbX ₂	R ₃ BiX ₂	R ₂ HfX ₂
UO ₂ (H ₂ O) ₂ ⁺²		

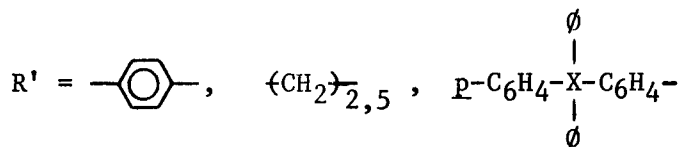
The method of polycondensation was found to be important in affecting polymer yield and molecular weight. Best results were usually obtained with the aqueous solution and normal interfacial systems for Group IVB containing systems and with the general nonaqueous systems for most of Group IVA systems. The latter system employs two immiscible organic solvents with the Lewis base component in the more polar solvent (e.g. nitrobenzene) and the Lewis acid component in the less polar solvent (e.g. hexane).

Several good candidates (XVI) were evolved which showed good thermal stability, but none coupled good physical properties or processability. The Pb (+4) polyester derived from diethyldichloride and tetrafluoroterephthalic acid retained 90% of its weight to 700°C (TGA, air) [112]. Isothermal aging at elevated temperatures was not reported.

Organometallic polymers have also been prepared by hydride addition reactions [113-116] typified in Equation (11).



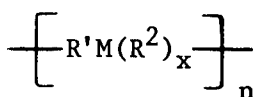
Where R = alkyl, phenyl
M = Sn, Si, Ge



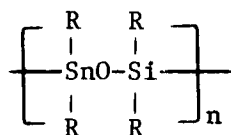
X = Ge, Sn, Sb

Products ranged from liquids to elastomers and low melting resins with reported molecular weights up to 100,000. In several cases the products were insoluble and infusible [115]. For a given series of polymers containing Sn the maximum amount of volatiles was released at 300-350°C, while those containing Si this maximum occurred at 500-520°C. The heat stability of polymers decreased in the series Si > Ge > Sn [115].

Organometallic polymers with structures (XVII) and (XVIII) [117-118] have also been prepared.



(XVII)



(XVIII)

Where R' = perfluorocarbon

M = transition metal

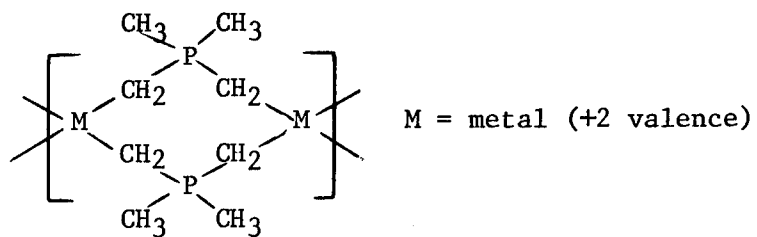
R² = carbonyl

x ≥ 1

R = alkyl, aryl or oxygen
bond to another Si atom

A typical polymer (XVII) (M = Fe, R' = C₄F₈, x = 4) was prepared by reacting Na₂Fe(CO)₄ with perfluoroadipoyl chloride in tetrahydrofuran [116]. This polymer was stable at 200°C. Polymers with repeating units of -Sn(R)₂OSi(R)₂- (R = C₁₋₁₈ hydrocarbon) were prepared by reaction of a disilanol (e.g. [(Ø)₂Si(OH)₂] with a substituted tin oxide or organotin dihalide [117]. The products varied from thermally stable liquids to thermoplastic solids. Increasing amounts of tin increased hardness and vitreous properties. Poly(organotin siloxanes) (XVIII) were prepared by double decomposition of the sodium salts of alkyl or aryl silanetriols and SnCl₄ [118]. Polymer properties were largely dependent on Sn content.

Metal dimethylphosphonium bis(methylide) polymers (XIX) were reported recently [119].



(XIX)

These polymers which were prepared from trimethylphosphorous methyllide $[(\text{CH}_3)_3\text{P}=\text{CH}_2]$ and an organometallic (R_2M) were hydrolytically unstable and decomposed at $180\text{--}200^\circ\text{C}$.

4.2.3 Bibliography

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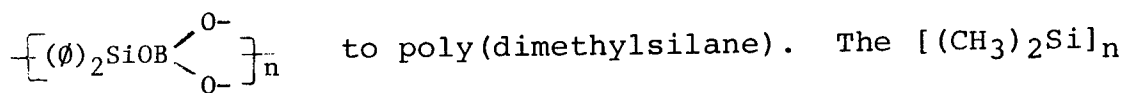
4.3 Polymers with Carbon and Non-Metal Backbone

4.3.1 Non-Carbon Side Groups

Many of the polymers in this section are structurally unrelated. Members include silicon carbide, polymers derived from phthalocyanine "sandwich" intermediates, carboranyl polymers linked through ester, formal, -S- or -P- groups, decaboranyl polymers, and polymers derived by condensation reactions of boron halides, boronic acids, or simple phosphorous compounds. Several of these polymers will be discussed in the text whereas other representative polymers and methods for their formation are presented in Table I.

Silicon carbide or carborundum (SiC) is unique. It is chemically inert, highly refractory, melts at 2600°C, and fibers have a tensile strength of 3×10^6 psi [1]. The very properties which make SiC unsuitable as a matrix resin for composites make it suitable as the reinforcing fiber. Fibers of SiC like boron nitride or graphite are light weight relative to steel and can serve as a reinforcement in composite materials at useful temperatures of 1100-2550°C. Traditional inorganic fibers such as glass and asbestos have excellent heat resistance to about 550°C but are degraded rapidly by continuous exposure to higher temperatures. Silicon carbide fibers, unlike graphite or boron fibers, offer excellent oxidation resistance.

Development of an economically attractive relatively flawless SiC fiber of sufficient length has been a problem. Recently, high tensile SiC fiber was prepared by heating a poly(carbosilane) precursor to 1300°C [2]. This method has promise for the mass production of continuous fiber. The requisite poly(carbosilane) was synthesized at atmospheric pressure by adding several weight percent of poly(borodiphenyl siloxane)

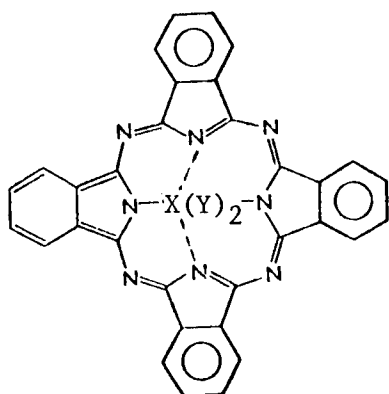


polymer* was prepared by dechlorination of dimethyldichlorosilane with sodium.

Poly(metal phthalocyanines) have been discussed in Section 4.2.1. Metal-free polymers containing the planar divalent tetradentate phthalocyanine (Pc) ligand have also been investigated as potentially thermally stable substances [3-11b]. The absence of metal is probably desirable because many polyvalent metals catalyze thermal or oxidative degradation.

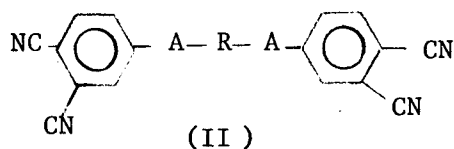
* See Section 4.3.2a for discussion of poly(carbosilanes).

Poly(phthalocyanines) lacking metal atoms are generally prepared by one of two routes, i.e., by use of a difunctional phthalocyanine monomer (I) or via a bis(phthalonitrile) intermediate (II). In polymers from (I) the backbone alternates oxygen with a non-metal and the phthalocyanine "sandwich" is



(I)

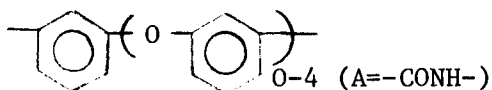
where X = Si, Ge
Y = Cl, OH



(II)

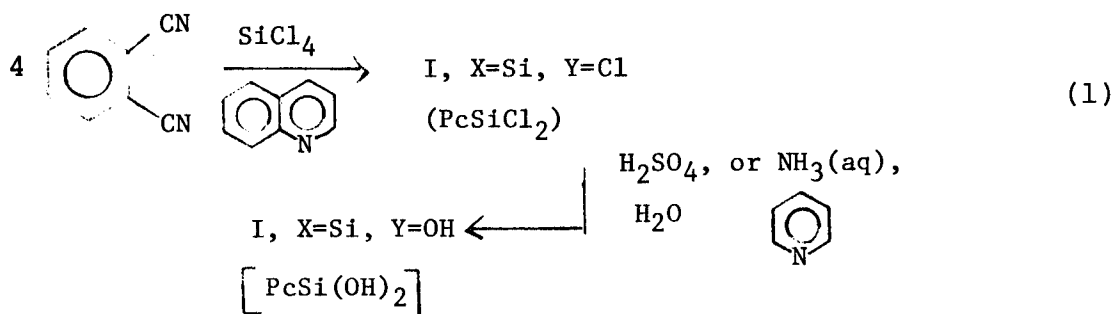
Where A = $\begin{array}{c} \text{O} \\ || \\ -\text{CNH}- \end{array}$, perfluoroalkylene (R is nil),
perfluoroalkylene ether (R is nil),
-N=CH-

R = $\{\text{CH}_2\}_x$ (A = -CONH-), arylene,



independently bonded to the non-metal.

Two members having the "sandwich" structure (I) were prepared as shown in Equation (1) [3-6a].



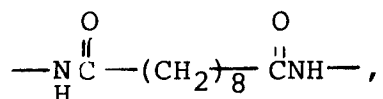
Germanium phthalocyanine dihydroxide was similarly prepared using GeCl_4 . PcSi(OH)_2 was dehydrated at 360-410°C to give a poly(siloxane), $\{\text{PcSiO}\}_n$, which was stable at 520°C in vacuo for several hours and required temperatures in excess of 550°C for decomposition [6b]. $\{\text{PcSiO}\}_n$ is very chemically stable [7]. It is unaffected by HF(aq.) at 180°C, refluxing aqueous

2M NaOH, and H₂SO₄ (room temperature). {PcGeO}_n is less stable and only withstands the caustic treatment. The tin containing {PcSnO}_n polymer is least stable and resists none of the above chemicals [7].

Metal-free poly(phthalocyanine-siloxanes) with organic groups bonded to silicon are discussed in Section 4.3.2e.

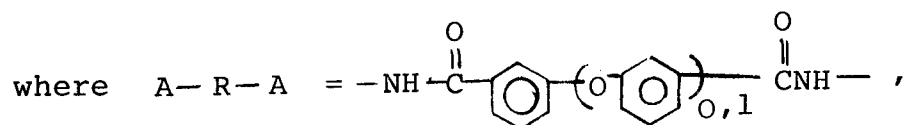
Polymers in which organic groups intervene between phthalocyanine and silicon have also been prepared [3,4,9]. Polymerization of PcSiCl₂ with resorcinol gave low molecular weight polymer [3]. Polymerization of PcSi(OH)₂ or its phthalocyanine silicon bis(pseudo halides) [(NCO)₂ or (NCS)₂] with bis(hydroxymethyl)_m-carborane gave low molecular weight condensation copolymer intermediates stable to about 360°C in air [4].

Polymers derived from the bis(phthalonitrile) intermediates (II) can be prepared readily by heating with ($\geq 200^\circ\text{C}$) or without (250–300°C) the presence of a metal (e.g., Cu or Sn⁺² in catalytic or stoichiometric amount for metal phthalocyanine formation) [10–11b]. These polymers with little or no metal are considered classical organic polymers and will be discussed only because of their close kinship to the polymers derived from intermediates (I). Most of the bis(phthalonitriles) (II) melt at about or below 300°C and can be cast or molded, a property desirable for the fabrication of composites. One resin prepared from (II), wherein the organic bridging ligand was



easily processed neat and was used to prepare moisture resistant composites which showed good retention of properties to about 240°C [10a]. The limiting factor in thermal stability appears to be the presence of amide groups and not the phthalocyanine structure.

The poly(phthalocyanines) prepared from (II),



possessed good retention of weight and strength after heating at elevated temperatures [10b]. No weight loss was observed on heating in air to 215°C for 569 hours. Heating 125 hours at 275°C + ca. 145 hours at 325°C led to ~10% weight loss in the metal-free system. No significant reduction in strength was observed after 100 hours at 325°C. Studies of copper-containing resins indicated that the metal is detrimental to good performance.

TABLE I

POLYMERS WITH CARBON AND NON-METAL ATOM BACKBONE
AND NO CARBON SIDE GROUPS

Example	Polymer Derivation	Probable Polymer Structure	Remarks
1 [12]	$\text{BX}_3 \text{ or } \phi\text{BCl}_2 + \text{H}_2\text{N-R-NH}_2$ + heat $\text{X} = \text{halogen}$ $\text{R} = \text{arylene, alkylene}$	$\left[\begin{array}{c} \text{B-NH-R-NH} \\ \\ \text{Z} \end{array} \right]_n$ $\text{Z} = \text{X}, \phi, \text{ or bond to another chain}$	Insol. and infusible, poor hydrolytic stability
2 [13]	$\text{BF}_3 + \text{BrMg} \langle \text{C}_6\text{H}_4 \rangle \text{MgBr}$	$\left[\begin{array}{c} \text{B} \\ \\ \text{Y} \end{array} \langle \text{C}_6\text{H}_4 \rangle \right]_n$ $\text{Y} = \text{F or bond to another chain}$	Viscous resin, hardened by heating to 270°C into brittle, glassy solid stable to 350°C.
3 [14]	$(\text{HO})_2\text{B-R-B}(\text{OH})_2 + (\text{HOCH}_2\text{CH}_2)_2\langle\text{CH}_2\rangle_{\text{X}}\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ + heat $\text{R} = \langle\text{CH}_2\rangle_4, \text{ } \langle\text{C}_6\text{H}_4\rangle$	$\left[\begin{array}{c} \text{N} \\ \nearrow \quad \searrow \\ \text{B-R-B} \end{array} \langle\text{CH}_2\rangle_{\text{X}} \right]_n$	$\text{R} = \text{alkylene, water sol.}$ $\text{R} = \text{phenylene, water insol. and stable to } 380^\circ\text{C.}$
4 [15]	$\text{HO} \langle\text{C}_6\text{H}_3(\text{OH})_2 \rangle \text{OH} + \text{H}_3\text{BO}_3$ 220-240°C	$\left[\begin{array}{c} \text{B} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \end{array} \langle\text{C}_6\text{H}_3(\text{OH})_2 \rangle \text{O-B-O} \right]_n$	Low mol. wt., dissolves in water with decomp., wt. retention of 99% & 92% at 500°C and 600°C, resp. (TGA).

TABLE I (Contd.)

POLYMERS WITH CARBON AND NON-METAL ATOM BACKBONE
AND NO CARBON SIDE GROUPS

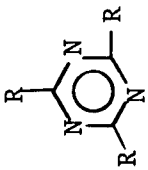
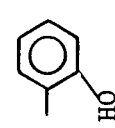
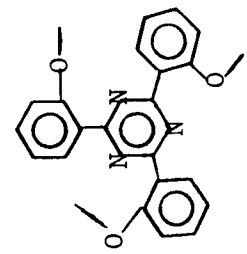
Example	Polymer Derivation	Probable Polymer Structure	Remarks
5 [16]	 $+ \text{H}_3\text{BO}_3 \text{ or } \text{ØB}(\text{OH})_2$ 200-500°C  R =	Polyborate linked via 	Heat resistant moldable linear or crosslinked materials; with $\text{ØB}(\text{OH})_2$ product stable to 380°C. Polymers can be filled with asbestos fiber or silica.
6 [17]	$\text{NC}(\text{CH}_2)_x\text{CN} + \text{B}_{10}\text{H}_{14}$ x > 2 (decaborane)	$-\text{[NC}(\text{CH}_2)_x\text{CN B}_{10}\text{H}_{12}]_n-$	Low mol. wt. high melting resin for x = 4 and thermoplastic softening at 80-100°C for n = 8.
7 [18]	$\text{M}_2(\text{BnHn}) + \text{ClC}(\text{R})=\text{CCl}$, polyphosphoric acid + P_2O_5 M = Na, NH_4 ; n = 10 or 12 R = alkylene, arylene	$\left[\text{(M)}_2(\text{BnHm}) \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{C} - \text{R} - \text{C} \\ \parallel \\ \text{O} \end{array} \right]_y \text{zH}_2\text{O} \right]_x$ m = (n-2), (n-4) y = 1, 2	Polymers useful as molding powders and ion-exchange resins.

TABLE I (Contd.)

POLYMERS WITH CARBON AND NON-METAL ATOM BACKBONE
AND NO CARBON SIDE GROUPS

Example	Polymer Derivation ^a	Probable Polymer Structure	Remarks
8 [19]	$(\text{HOCH}_2\text{CH}_2\text{CB}_{10}\text{H}_{10}\text{C}-\text{CH}_2)_2\text{O}$ $(\text{CH}_2\text{O})_n + \text{H}^\oplus$	$-\text{[O-R-OCH}_2\text{]}_n-$ $\text{R} = \text{[CH}_2\text{CH}_2\text{CB}_{10}\text{H}_{10}\text{CCH}_2\text{]}_2\text{O}$	Polyformal, brittle, softening at 63°C.
9	$\text{HOCH}_2\text{-CB}_{10}\text{H}_{10}\text{C-CH}_2\text{OH}$ or $[\text{HO-CH}_2\text{]}_{1,2}\text{-CB}_{10}\text{H}_{10}\text{CCH}_2\text{O}$ + diacid or diacid chloride	Conventional polyester structure.	Polyesters ranged from viscous liquids to substances with T_m of 310°C.
10 [21]	(a) $\text{ClS-CB}_{10}\text{H}_{10}\text{C-SCl} + \text{LiCB}_{10}\text{H}_{10}\text{Cl}$ (b) $\text{ClS-CB}_{10}\text{H}_{10}\text{C-SCl} + \text{C}_2\text{H}_5\text{OH (reflux)}$ (c) $\text{ClS-CB}_{10}\text{H}_{10}\text{C-SCl} + \text{H}_2\text{O (reflux)}$	$-\text{[S-CB}_{10}\text{H}_{10}\text{C-}]_n-$ $-\text{[S-CB}_{10}\text{H}_{10}\text{C-S-}]_n-$ $-\text{[S-CB}_{10}\text{H}_{10}\text{C-S(O)-}]_n-$ (a polythiol sulfinate)	All m-carborane polymers low to modest mol. wt. [5,400 for (a)] melting at 210-310°C; using p-carborane polymer (a) had m.p. >420°C.

^a $\text{CB}_{10}\text{H}_{10}\text{C} = \text{---C---}$
 $\text{B}_{10}\text{H}_{10}$, m-carboranyl

TABLE I (Contd.)

POLYMERS WITH CARBON AND NON-METAL ATOM BACKBONE
AND NO CARBON SIDE GROUPS

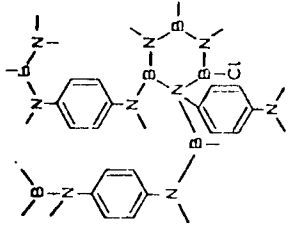
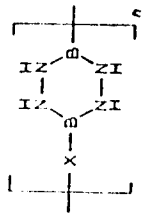
Example	Polymer Derivation ^a	Probable Polymer Structure	Remarks
11 [22]	$\text{R}-\text{CB}_{10}\text{H}_{10}\text{C}-\text{R}' + (?)^b$ $\text{R} = -\text{C}_6\text{H}_4\text{N}(\text{NO})\overset{\text{O}}{\underset{ }{\text{C}}}\text{CH}_3, \quad \text{R}' = \text{H or R}$	--	Monomers for synthesis of heat-stable polymers.
12 [23a,b]	(a) $\text{LiCB}_{10}\text{H}_{10}\text{Cl}_4 + \text{PCl}_3$ (b) $\text{LiCB}_{10}\text{H}_{10}\text{Cl}_4 + \text{COCl}_2$	$-\text{CB}_{10}\text{H}_{10}\text{PCl}_2-$ $-\text{CB}_{10}\text{H}_{10}\text{C-CO}-$	Degree of polymerization was 5.
13 [24]	$\text{PO}(\text{NH}_2)_3 + \text{heat}$	$-\text{PON}-_x$ (phosphorus oxynitride)	Melts $>1,000^\circ\text{C}$ to give glass-like substance; stable to dil. acids and alkalis, hydrolyzed at 200°C .
14 [25]	$\text{PH}_3 + \text{B}_2\text{H}_6$	$[\text{H}_{<2}\text{PBH}_{<2}]_n$ (phosphinoborane)	White unstable solid, rapid dec. by water or heating to 200°C .

^a $\text{CB}_{10}\text{H}_{10}\text{C} = -\text{C}-\overset{\text{O}}{\underset{\text{B}_{10}\text{H}_{10}}{\text{C}}}-$, m-carboranyl

^b Unavailable from Chem. Abstr.

TABLE I (Contd.)

POLYMERS WITH CARBON AND NON-METAL ATOM BACKBONE
AND NO CARBON SIDE GROUPS

Example	Polymer Derivation	Probable Polymer Structure	Remarks
15 [26]	$ \begin{array}{c} \text{R}_2\text{N} \quad \text{NR}_2 \\ \diagdown \quad \diagup \\ \text{B} - \text{B} \\ \diagup \quad \diagdown \\ \text{R}_2\text{N} \quad \text{NR}_2 \end{array} + 2 \text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2 $ <p style="text-align: center;">(m-qr-p-)</p>	$ \left[\text{NH}-\text{C}_6\text{H}_4-\text{NH}-\text{B} \right]_n $	Intractable, high thermal stability.
16 [26]	$ \begin{array}{c} \text{H} \\ \\ \text{Cl}_4\text{B}^- + \text{H}_3\text{N}-\text{C}_6\text{H}_4-\text{NB}^+\text{Cl}_2 \\ \\ \text{Heat in C}_6\text{H}_5\text{Cl} \end{array} $		Infusible, insol. powders, v. low bulk densities; thermally stable but easily hydrolyzed.
17 [26]	$ \text{H}_2\text{N}-\text{NH}_2 + (\text{HO})_2\text{B}-\text{C}_6\text{H}_4-\text{B}(\text{OH})_2 $ <p style="text-align: center;">or pyroboric acid tetraacetate</p>		--

(where X = p-C₆H₄ or -O-)

TABLE I (Contd.)

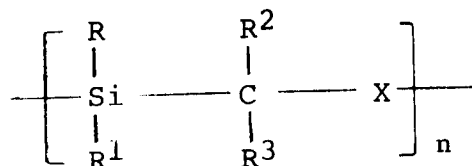
POLYMERS WITH CARBON AND NON-METAL ATOM BACKBONE
AND NO CARBON SIDE GROUPS

Example	Polymer Derivation	Probable Polymer Structure	Remarks
18 [26]	$C_4H_8(NH)_2 + 2(CH_3)_2NB_2H_5$ (piperazine) 200°C		Vaporizes upon heating in vac. at 240-250°C.
19 [26]	Pyrolysis of hydrazine-borane		Resistant to hydrolysis; decomp. slowly at $\geq 200^\circ C$.
20 [26]	$F_2BNR_2 + \text{heat}$ (R = CH_3 , C_2H_5)		For R = C_2H_5 , mol. wt. 10,000-12,000; air stable, sol., decomp. slowly in H_2O and rapidly in aq. alkali.

4.3.2 Carbon Side Groups

(a) Poly(carbosilanes)

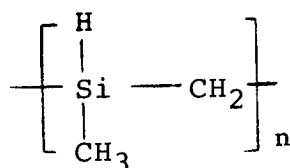
This class of materials can be represented by the general formula



where R, R¹, R², and R³ = H, alkyl, aryl

X = alkylene, arylene, or covalent bond.

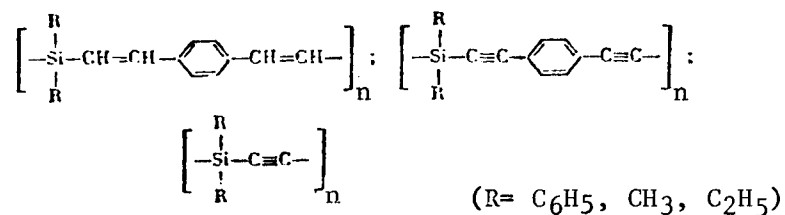
On the basis of relative bond energies (Si-C = 78 kcal/mol vs Si-O = 106 kcal/mol) [27] one would expect poly(carbosilanes) to be less stable than the corresponding siloxane. However, linear silylmethylene polymers have been prepared [28-30] which exhibit superior thermal stability (T_m=340°C) to poly(dimethylsiloxanes). Poly(dimethylsilane), as hexamer or linear polymer, can be converted at 300-500°C to high molecular weight poly(carbosilane),



which can then be spun into fiber [31]. These fibers in turn can be thermally oxidized to yield fibrous β-silicon carbide (Section 4.3.1).

More recently [32] report has been made of linear copolymers, derived from the reaction (Na/K, THF) of phenylmethyldichlorosilane and dimethyldichlorosilane, which are stable in air at 350°C and which do not undergo the "unzipping" reaction. By varying the phenyl content of these polymers one is able to control crystallinity, solvent solubility, and melting point.

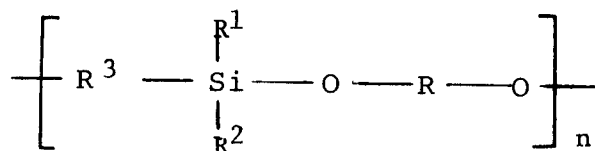
Polymers of the type



have been prepared [33-35] and these materials show no weight loss below 450-550°C, but the most interesting candidates in this class are the poly(silarylenes) which are critically reviewed in Section 5.3.

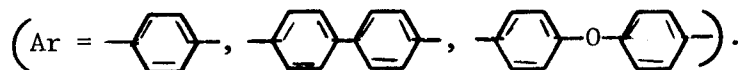
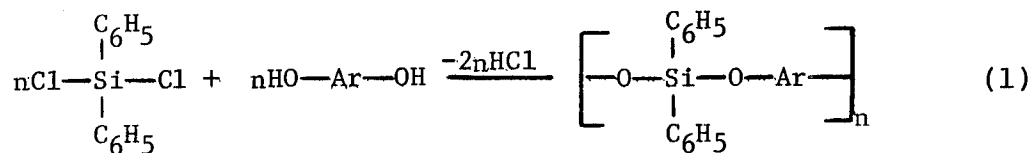
(b) Poly(carbosiloxanes)

This class of siloxane polymers can be represented by the general formula

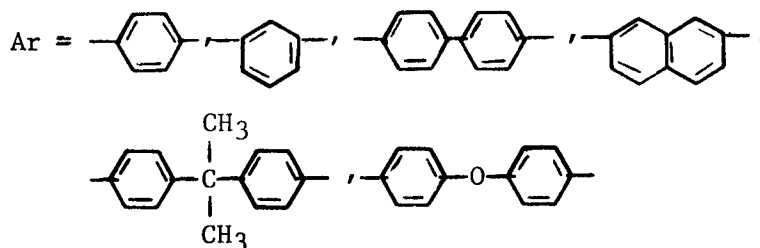
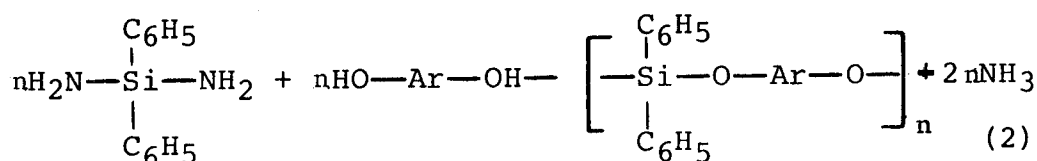


R^1 & R^2 = alkyl or aryl
 R^3 = arylene or alkylene
 R^3 = covalent bond, R, or silylarylene

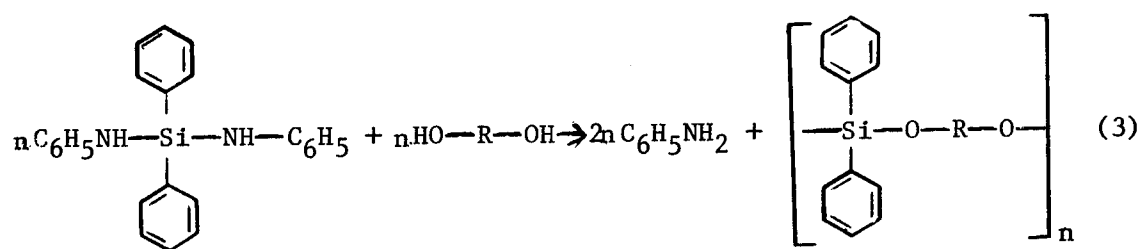
Considerable attention has focused upon the linear condensation products derived from the reaction of bis-phenols and dialkyl or diaryl dichlorosilanes [36] (Equation 1).



An alternate synthesis route involves the reaction of silyl-diamines with various bis-phenols [37-38] according to Equation (2).



Polycondensation of diols and bis-(anilino)-diphenylsilane also yields polyesters of diarylsilicic acids and corresponding diols, Equation (3) [39].



The polymers derived from this reaction possess high heat resistance (Table I and Figure 1) and are good fiber formers [37].

TABLE I
PROPERTIES OF POLYESTERS OF DIPHENYLSILICIC ACID
[37]

Formula of Repeating Unit	T _m , °C
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{---Si---O---} \langle \text{benzene ring} \rangle \text{---O---} \\ \\ \text{C}_6\text{H}_5 \end{array}$	>300
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{---Si---O---} \langle \text{benzene ring} \rangle \text{---O---} \\ \\ \text{C}_6\text{H}_5 \end{array}$	240-245
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{---Si---O---} \langle \text{benzene ring} \rangle \text{---} \langle \text{benzene ring} \rangle \text{---O---} \\ \\ \text{C}_6\text{H}_5 \end{array}$	>300
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{---Si---O---} \langle \text{naphthalene ring} \rangle \text{---O---} \\ \\ \text{C}_6\text{H}_5 \end{array}$	123-125
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{---Si---O---} \langle \text{benzene ring} \rangle \text{---C---} \langle \text{benzene ring} \rangle \text{---O---} \\ \quad \\ \text{C}_6\text{H}_5 \text{C}_6\text{H}_5 \end{array}$	99-100
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{---Si---O---}(\text{CH}_2)_4\text{---O---} \\ \\ \text{C}_6\text{H}_5 \end{array}$	253-257

TABLE I (Contd.)

PROPERTIES OF POLYESTERS OF DIPHENYLSILICIC ACID
[37]

Formula of Repeating Unit	T_m , °C
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{---Si---O---} \langle \text{---} \rangle \text{---O---Si---} \begin{array}{c} \text{C}_6\text{H}_5 \\ \end{array} \\ \\ \text{C}_6\text{H}_5 \end{array}$	>300
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{---Si---O---} \langle \text{---} \rangle \text{---O---} \langle \text{---} \rangle \text{---O---} \\ \\ \text{C}_6\text{H}_5 \end{array}$	127-130

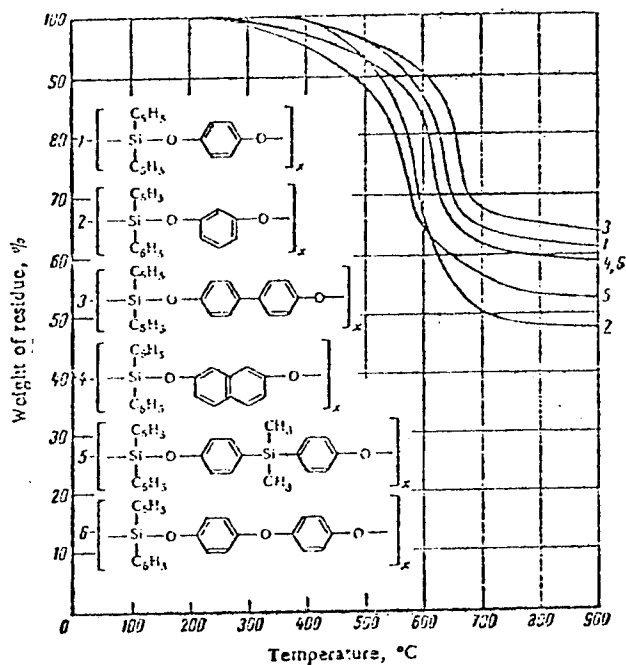
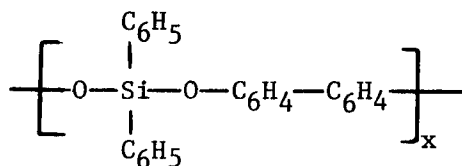


Figure 1.

Dynamic Thermogravimetric Analysis of Polyesters of Diphenylsilicic Acid. Rate of Heating 4 degrees/minute, in Nitrogen Atmosphere [37].

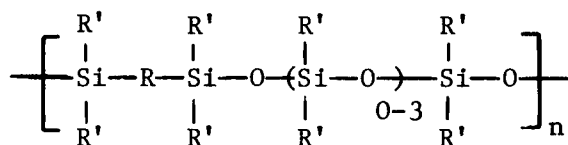
Poly-(4,4'-bis-oxy-biphenylene)diphenylsilane



forms films which are cured by heating 3 hours at 298°C. Films aged 100 hours at 427 and 538°C lost 10 and 13% of their weight, respectively. Films with added aluminum can be held unaltered for 25 hours at 427, 478, and 538°C without losing their color or adhesive properties.

Activity in this field remains high as evidenced by the large number of recent publications [39-54]. Yet, in spite of excellent thermal stability characteristics, these materials, with the exception of the poly(silarylene-siloxanes) which are critically reviewed in Section 5.2, suffer from poor hydrolytic stability and are therefore excluded from further consideration.

Poly(carbosiloxanes) of the type

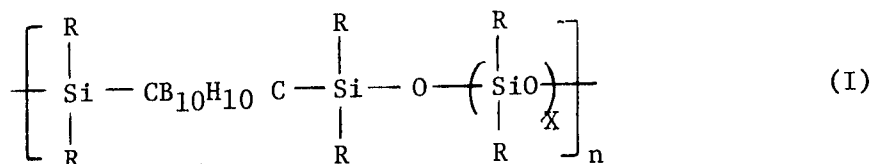


R' = alkyl, aryl
R = arylene, carboranyl

were prepared by a bis(ureido)silane-diol (including disilanol) condensation [55-57a,b] (also see Sections 4.3.2c and 5.2). Although this polycondensation has afforded very high molecular weight polymers it suffers from two drawbacks; first, the bis(ureido) reagent is easily decomposed; second, the polymerization has been found difficult to reproduce [55-56].

(c) Poly(Carborane-Siloxanes)

Poly(carborane-siloxanes) discussed in this section will be defined by the general formula (I). Other carborane containing polymers are discussed in Sections 4.3.2c, d.



where R = CH₃ (67-100% of R's),
 C₆H₅ (up to 33% of R's),
 CH₂ = CH-, CF₃CH₂CH₂-
 X = 1-5

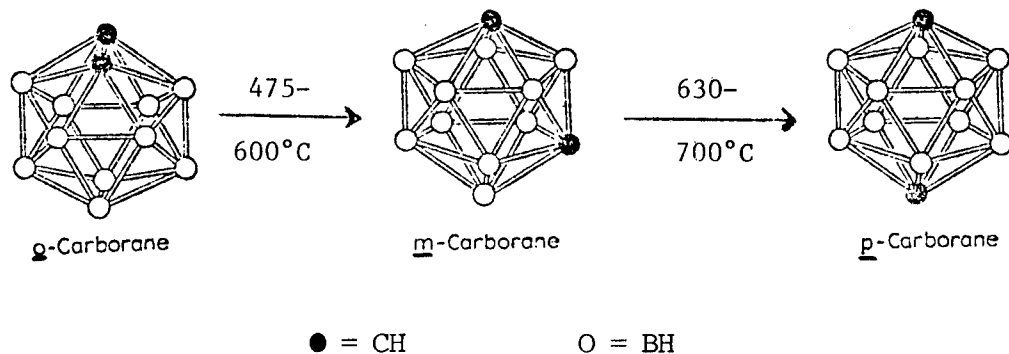
Poly(carborane-siloxanes) have been actively researched for at least the last 12 years and have been the subject of several reviews [58-60]. The strong interest has been due primarily to the superior thermal stability of carborane-siloxanes compared to conventional silicones. The objective of most, if not all, of the efforts was to evolve a superior elastomer useful over a broad temperature range including 600°F (315°C).

The development of poly(carborane-siloxane) elastomers has clearly been a technical success, therefore this class will be discussed at length in this section. Poly(carborane-siloxanes) were considered seriously for critical review but were eventually abandoned from consideration for three reasons. First, they offer only about a 50°C gain in temperature serviceability over the better currently available poly(siloxanes). Second, the polymers would be extremely costly because of the high cost of dodecacarborane, estimated at about \$200/lb. and \$100/lb. at volume productions of 100,000 lbs. and 1 million lbs. per year, respectively. The polymer cost would approximate the decacarborane cost because of dilution with the less expensive siloxanyl moiety. Third, replacement of the carboranyl unit by selected arylene or heteroarylene groups should afford polymers of comparable stability and probably with higher physical transition temperatures.

Properties of carborane polymers, like conventional silicones, can be structurally modified via the appropriate pendant groups. Specifically, transition temperatures, stability, and solvent resistance can be tailored to a large degree. The polymer series (I) where x is 1 have received the greatest attention because of the optimum balance of elastomeric properties and thermal stability.

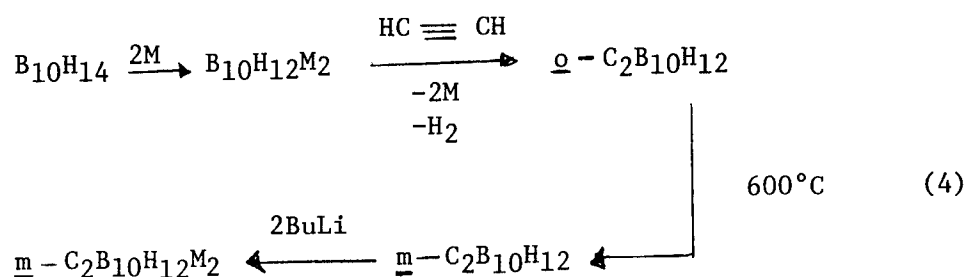
Poly(carborane-siloxanes) have found limited commercial utility. Currently, they are being used as the liquid phase for high temperature gas chromatography [61]. Carborane-siloxanes can be fabricated into O-rings, gaskets, and wire coverings which are capable of performing at temperatures above 300°C [62,63]. An improved electrical insulation material based on mica and poly(carborane-siloxane) has been reported [64]. Poly(carborane-siloxane) ("Dexsil 300") impregnated mica sheet after curing gave 0.07% weight loss after exposure to test cycle of 1250°F (677°C).

One of the better approaches to prepare high temperature inorganic based elastomers has been the development of carborane-siloxane polymers. The marriage of carborane and siloxane backbones has significantly increased thermal stability [65]. Of several carborane families (CB_nH_n+2 , CB_nH_n+4 , $\text{C}_2\text{B}_n\text{H}_n+2$, etc.), the dicarbo-closo-dodecacarborane-12, $\text{C}_2\text{B}_{10}\text{H}_{12}$, has been studied intensively [65,66]. $\text{C}_2\text{B}_{10}\text{H}_{12}$ has an icosahedral structure and exists as three interconvertible isomers as shown.



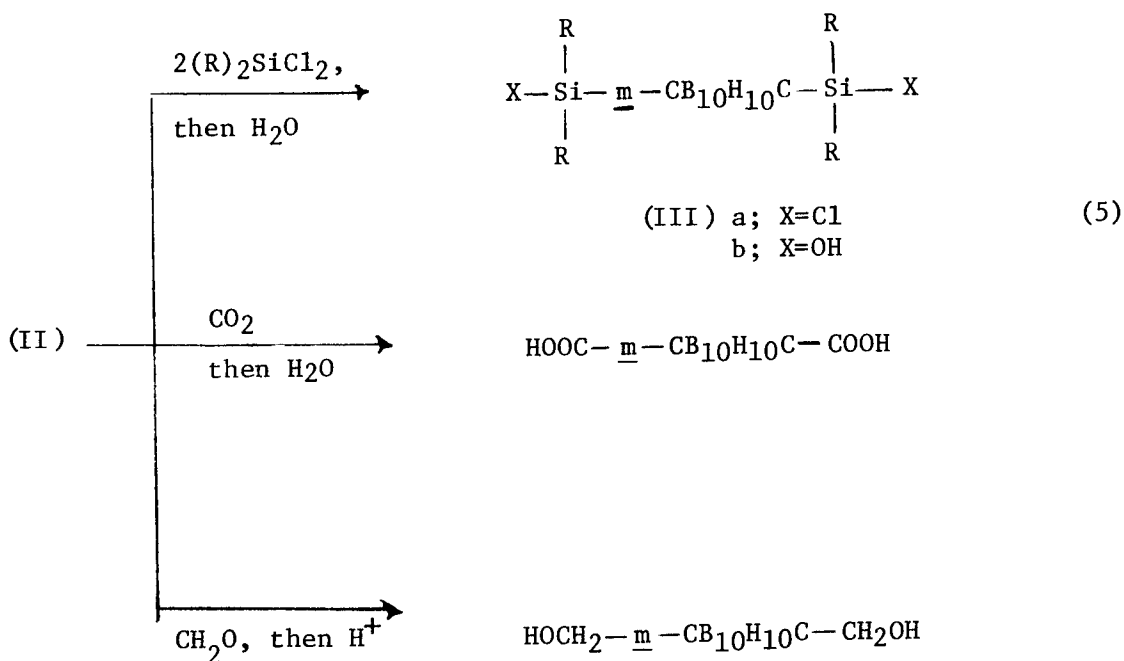
The para isomer is the most stable, most difficult to obtain, and potentially the most expensive. All other things being equal, polymers derived from the para isomer afford the highest physical transition temperatures. Unless stated otherwise, the polymers in this section are derived from m-carborane.

Dicarbo-dodecacarborane has been prepared and converted to bifunctional polymer intermediates by reaction of the dialkali salt as shown in Equations (4)-(5):

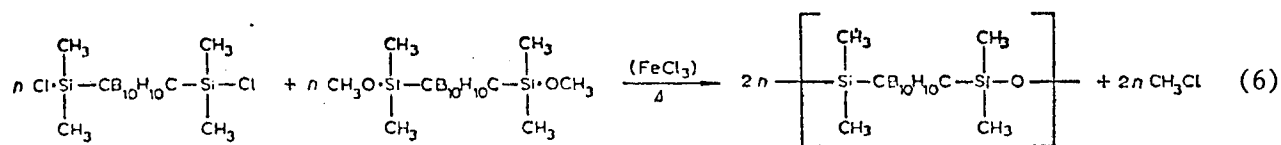


(II)

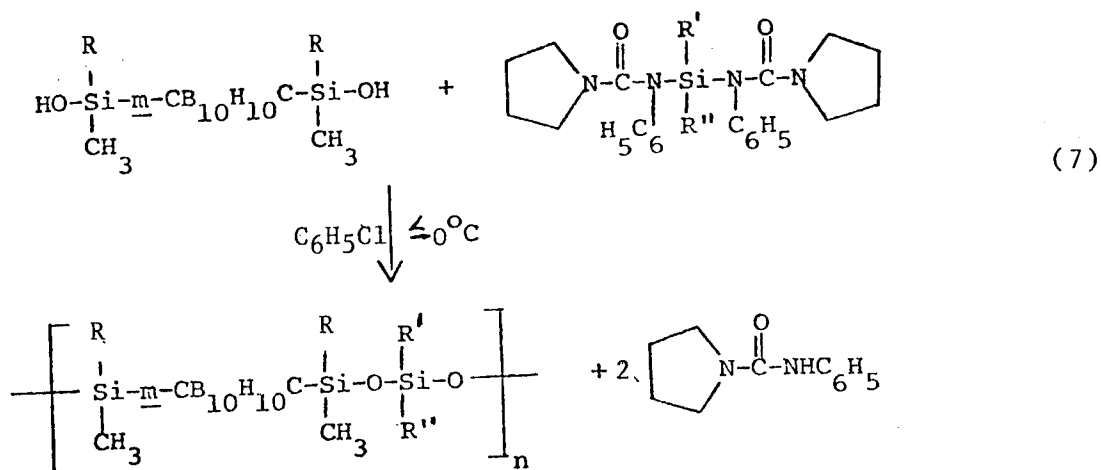
where M = Lewis base (e.g., Li, Na)



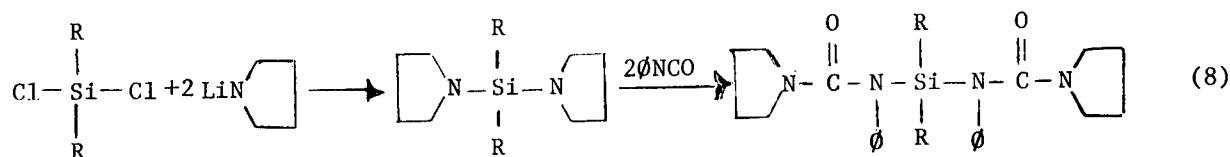
Ideally, self condensation of (III b) or reaction of (III a) should afford high molecular weight poly(carborane-siloxane). Polymer (I), $x=0$, $R' = CH_3$ could not be prepared by polymerization of the disilanol (III b) ($R=CH_3$) [65]. This relative inertness was attributed to the extremely electronegative carborane nucleus [67]. In general, functional groups attached directly to the carborane nucleus behave chemically as though bonded to an electron-withdrawing group with a large steric requirement and high stability. The desired polymer was prepared [65] as shown in Equation (6).



Crosslinked polymer (I), $x=1$, $R=CH_3$ [68,69] was similarly prepared [65] by reaction of (III b) with $(\text{CH}_3)_2\text{Si}(\text{Cl})_2$. Crosslinking catalyzed by FeCl_3 was circumvented by reaction of (III b) ($R=CH_3$) with silyldiamines, e.g. $(\text{CH}_3)_2\text{Si}(\text{NR}_2)_2$. However, low molecular weights (M_w 18,000) were obtained because of dimethylamine induced cleavage of the carborane-silicon bond [55]. This problem was resolved by the use of silyl urea intermediates such as bis(N-phenyl-N-tetramethylene ureido)silanes (Equation 7). The by-product urea leaving group is essentially non-nucleophilic and leads to no Si-carborane cleavage. High molecular weight carborane-siloxane polymers, i.e. greater than one million, were prepared by this technique [55,56].

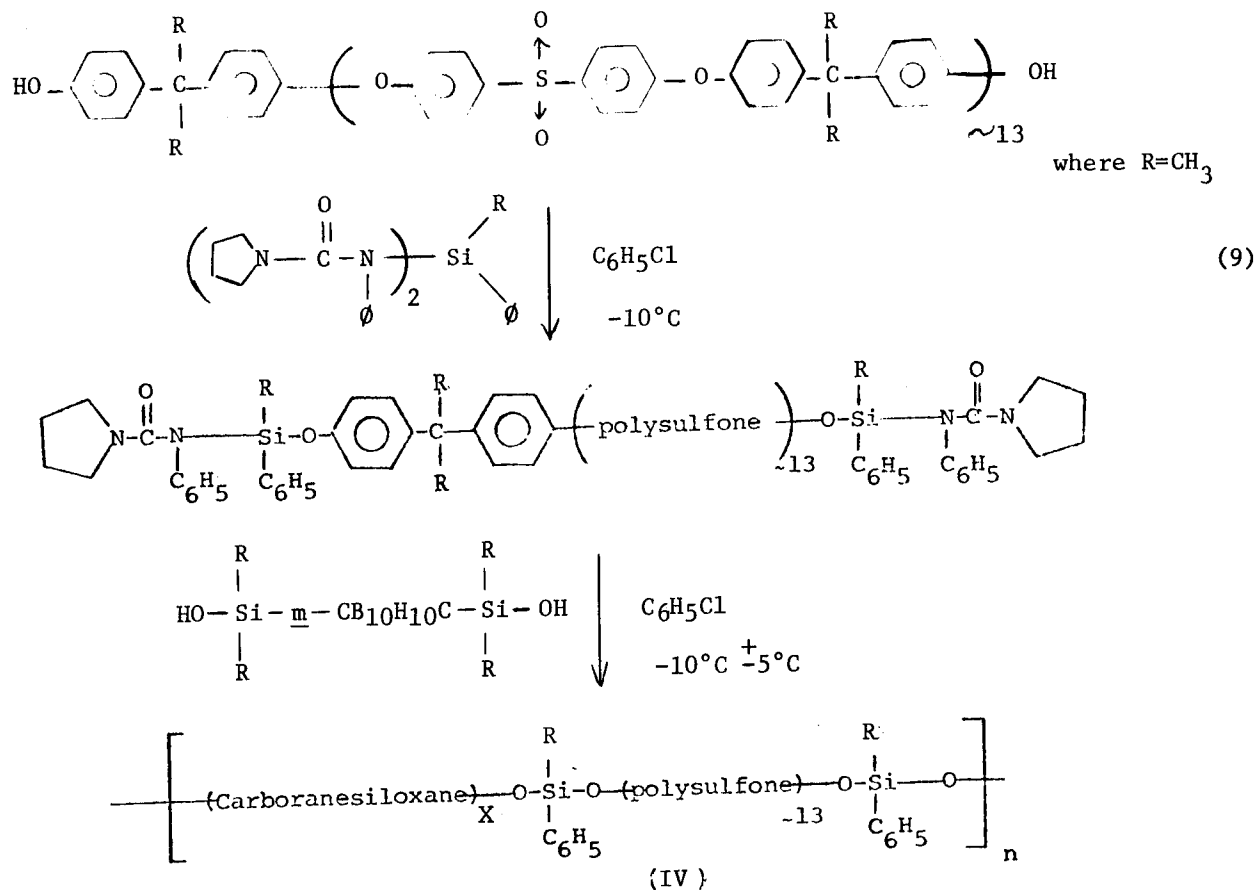


The ureido silane reactant was conveniently prepared [55,56] as shown in Equation (8).

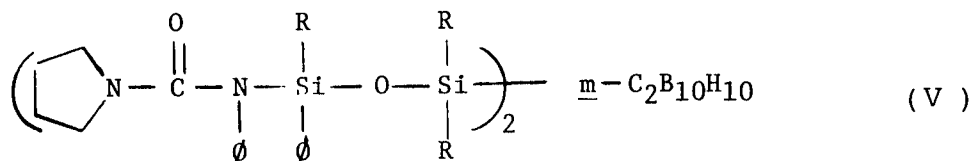


Polycondensation via the ureido intermediates have several disadvantages; the bis(ureido)silane is costly relative to dichlorosilane and is extremely moisture sensitive. More importantly, the polymerization to very high molecular weight polymer has been irreproducible [56].

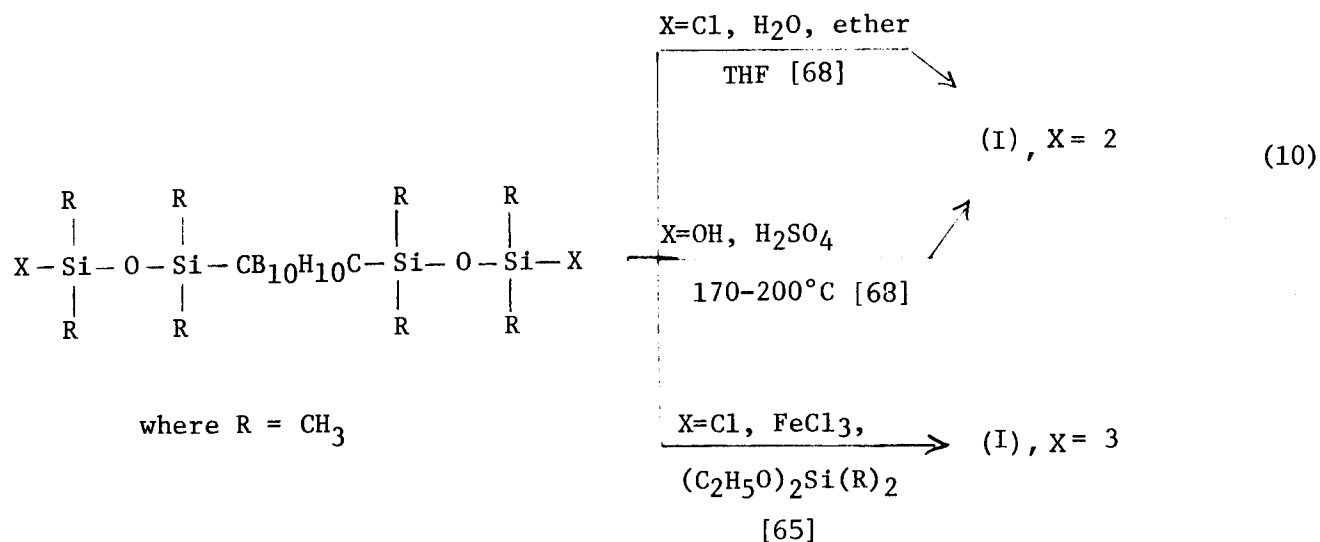
Block copolymers (IV) wherein the blocks consist of poly(carborane-siloxanes) ("soft" block) and polysulfone ("hard" block) have also been prepared using a ureidosilane-silanol polycondensation reaction as shown in Equation (9) [56].



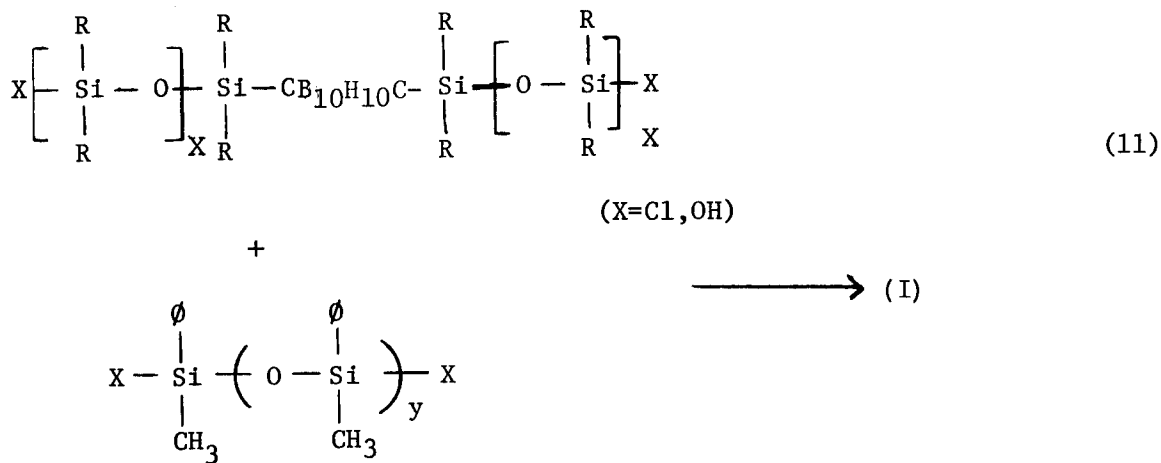
Similarly, the hydroxyl terminated polysulfone was condensed with a ureidosilane modified m-carboranedisilanol (V) to afford a random block copolymer.



Lower molecular weight carborane-siloxanes (I) where $x=2$ were also prepared via conventional siloxane condensation processes as shown in Equation (10).



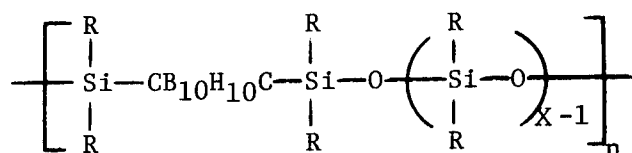
Cohydrolysis was used to prepare carborane-siloxanes containing phenyl groups [68] bonded to silicon (Equation 11).



$y = \text{zero to } 2$

Groups other than phenyl can also be incorporated by similar cohydrolysis reactions. Methyltrifluoropropylsiloxane groups improve solvent resistance [70] whereas methylvinylsiloxane sites facilitate vulcanization and optimization of physico-mechanical properties.

Physical transitions determined by Torsional Braid Analysis (TBA) [71,72] for some linear carborane-dimethyl siloxanes



(R = CH₃, X = 1-5)

show several trends:

- (1) Both T_m (or T_{cryst.}) and T_g increase with decreasing n values.
- (2) Para carboranes give higher transition temperatures than meta carboranes (+33°C increase in T_g, +70°C increase in T_m for n=3).
- (3) Effect of greatly increasing molecular weight for n=3 was to eliminate T_m or T_{cryst.} but had essentially no effect on T_g.

Some selected transitions as determined by DSC [73] are shown in Table II.

TABLE II
PHYSICAL TRANSITION TEMPERATURES OF SELECTED
POLY (CARBORANE-SILOXANES) [73]

Carborane	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{---Si---CB}_{10}\text{H}_{10}\text{C---Si---O---} \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{---Si---O---} \end{array} \right)_{X-1} \\ \\ \text{CH}_3 \end{array} \right]_n$	T _m (°C)	T _g (°C)
	R R'		
meta	CH ₃ CH ₃	68, 90	-50
para	CH ₃ CH ₃	220	Not determined
meta	C ₆ H ₅ C ₆ H ₅	Absent	22
meta	CH ₃ C ₆ H ₅	Absent	-12

Generally, a linear relationship is obtained [71] for homologous series of carborane-siloxanes, by considering their structures to be an alternating copolymer of $\text{-CB}_{10}\text{H}_{10}\text{CSi}(\text{CH}_3)_2\text{-}$ and $\text{[Si(R)}_2\text{-O]}_x$ linkages by plotting weight fraction of $\text{-CB}_{10}\text{H}_{10}\text{CSi}(\text{CH}_3)_2$ vs $1/T_g$.

The unique property of carborane-siloxane elastomers compared to conventional siloxanes such as poly(dimethylsiloxane) is their improved thermal stability. Undoubtedly, incorporation of the carborane moiety increases resistance towards reversion to cyclic siloxane oligomers at elevated temperatures (See also Section 4.1.2a). Most of the thermal studies have employed thermal gravimetric analysis (TGA) in an inert atmosphere and indicate

1. Weight retention to 800°C by TGA decreases linearly as length of $\text{Si}(\text{CH}_3)_2\text{-O-}$ chain is increased [71].
2. DTA and DSC showed no indication of reactions to $500\text{--}550^\circ\text{C}$ [65,71].
3. Addition of *m*-carborane to siloxane chain impedes siloxane chain depolymerization [74]. Several polymers showed competing reactions, chain degradation leading to oligomers and rupture of Si-C and C-H bonds liberating hydrogen and methane and crosslinking [74].
4. Substitution of methyl groups by phenyl leads to increased weight retention (up to 43%) at 800°C (via TGA) [68,71,74]. One study indicated phenyl groups lead to crosslinking; therefore, less weight loss on heating [74]. Temperature at which onset of weight loss occurs increases ($45\text{--}50^\circ\text{C}$) with methylphenyl content.
5. Substitution of methyl groups by trifluoropropyl increases weight loss and lowers the temperature at which onset of weight loss occurs [70,75].
6. Onset of thermo-oxidation (by DSC) occurs at about 330°C in all *m*-carborane-dimethylsiloxane polymers [65].
7. Ultra-high molecular weight polymer ($\bar{M}_w = 2,230,000$) showed a 4% weight gain up to 800°C (TGA, air) [56]. Apparently oxidative crosslinking more than compensates for degradative chain scission processes.

Of interest is the fact that poly(carborane-dimethylsiloxane) when compared to poly(dimethylsiloxane) appears to be more oxidatively stable by DTA and TGA and less stable by TGA studies.

Carborane-siloxanes can be compounded and crosslinked using conventional silicone technology [63,76]. Use of siliceous reinforcing fillers led to property improvement [62,63,77,78].

The dramatic effect of molecular weight on properties is quite pronounced as seen in Table III. An increase in polymer molecular weight (\bar{M}_w) from 150,000 to 250,000 raised the elongation at break from 14 to 550% for a 33% methylphenyl modified polymer and from 60 to 700% for a 33% diphenyl modified polymer [56,70],

Ferric oxide has proven to be an effective antioxidant stabilizer for carborane-siloxanes [56,74]. Some elastomeric properties of a phenyl-modified vulcanizate containing ferric oxide (prepared by in situ thermal decomposition of iron pentacarbonyl) were retained after 1,000 hours air aging at 315°C [56,74]. Without ferric oxide embrittlement occurred after 150 hours.

The effect of polymer structure on vulcanizate properties is predictably as follows; lower siloxane content [79] and higher phenyl content [62] increase high-temperature potential.

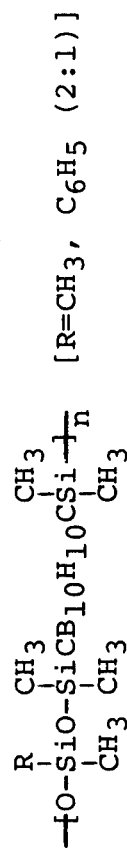
Heat aging at 315°C (N_2) results in a decrease in modulus, tensile, and elongation at break [74]. This was attributed to thermal breaking of crosslinks. The deterioration of properties in air at 315°C is believed to be due to a combination of cleavage of crosslinks and oxidative bond forming processes. Heat aging in air at higher temperatures results in greater property deterioration as shown in Table IV.

Heat aging poly(carborane-siloxane) [I, where $X = 1$, $R = CH_3(2/3)$, $\phi(1/3)$] in nitrogen 24 hours at 340°C resulted in partial thermal crosslinking whereas at 370°C the stock is totally crosslinked. This is probably indicative of bond forming processes at these temperatures and leads to the important suggestion that the practical long-term temperature limit of these particular vulcanizates is about 315°C and the short term limit is 340°C [74,81].

Hydrolytic stability of poly(carborane-siloxane) [I, where $X = 1$, $R = CH_3(2/3)$, $\phi(1/3)$] is good [63]. Exposure of a vulcanizate to 91% humidity at 38°C for two weeks did not deteriorate properties. Immersion in water for one week at ambient temperature and one day at 100°C showed no significant change in tensile strength or elongation. Resistance to common organic solvents has also been studied [63,76]. The data show small changes in mechanical properties but large volume changes (>100%) in certain solvents (toluene, xylene, carbon tetrachloride, ASTM Fuel B). These effects are similar to silicon rubber [63].

TABLE III

MECHANICAL PROPERTIES OF UNCURED POLY (CARBORANE-SILOXANE)



AS A FUNCTION OF MOLECULAR WEIGHT [56]

Reduced Viscosity ^a (dL/Gm)	0.53	0.98	1.50	2.55	3.64	5.12
Molecular Weight ^b (\bar{M}_w)	146,100	378,600	644,000	1,681,000	2,230,000	5,116,000
Young's Modulus (psi)	5,300	4,290	4,100	3,635	4,700	2,800
Tensile Strength (psi)	192	251	750	752	695	680
Elongation at Break (%)	20	30	410	300	450	600
Yield Strength (psi)	none	163	290	193	207	106
Yield Elongation (%)	none	30	13	25	15	20
Melt Flow (°C)	~50	~50	~90	none	none	none
Melt Failure (°C)	~90	~100	~190	none	none	none

^a Reduced viscosity in CHCl₃ at 25°C.^b Molecular weight by GPC.

TABLE IV

MECHANICAL PROPERTIES OF A 33 MOLE PERCENT METHYLPHENYL-MODIFIED
CARBORANE-SILOXANE VULCANIZATE AT 25°C AND AFTER HEAT AGING IN AIR

[74,80.]

Aging Time/Testing Temp. (hrs)	Young's Modulus (psi)	Tensile Strength (psi)	Elongation at Break (%)
↑ 0 ↓ 315°C Aging 0 50 150 ↓ 300 300 300	533 1,117 1,813 730 1,170 1,820	613 427 533 70 115 230	100 55 45 13 12 13
↑ 343°C Aging 0 16 ↓	430 952	740 503	220 50
↑ 371°C Aging 0 4 ↓	430 15,600	740 839	220 15

(d) Non-Siloxane Carborane Polymers with Carbon Side Groups

Several carboranyl polymers with carbon side groups have been reported which are not linked by siloxanyl or metal atoms. These polymers are linked by non-metal atoms such as nitrogen, phosphorus, and germanium as shown in Table V.

Table V

Carboranyl Polymers Linked by N, P, Ge and Containing Carbon in Side Groups

Ex.	Polymer Derivation	Polymer Structure	Remarks
1. [82]	$\text{LiCB}_{10}\text{H}_9\text{BrCLi} + \text{PCl}_3 + \text{CH}_3\text{OH}$ (brominated <u>m</u> -carborane)	$\begin{array}{c} \text{Cl} \\ \\ \text{+CB}_{10}\text{H}_9\text{BrC}-\text{P}- \\ \\ \text{-CB}_{10}\text{H}_9\text{BrC}-\text{P}- \\ \\ \text{OCH}_3 \end{array} \text{+}_n$	No particularly interesting properties
2. [59a]	$\text{LiCB}_{10}\text{H}_{10}\text{CLi} + (\text{R})_2\text{GeCl}_2$	$\text{+ CB}_{10}\text{H}_{10}\text{C Ge(R)}_2 \text{+}_n$	$n = 26$ Also prepared co-polymer with $(\text{CH}_3)_2\text{SnCl}_2$
3. [59a]	$\begin{array}{c} \text{R} \\ \\ \text{ClGe}-\text{CB}_{10}\text{H}_{10}\text{C}-\text{Ge}-\text{Cl} \\ \\ \text{R} \end{array} + \text{NH}_3$	$\begin{array}{c} \text{R} \qquad \qquad \text{R} \\ \qquad \qquad \\ \text{+ Ge}-\text{CB}_{10}\text{H}_{10}\text{C}-\text{Ge}-\text{NH}- \\ \qquad \qquad \\ \text{R} \qquad \qquad \text{R} \end{array} \text{+}_n$	Stability to $\geq 450^\circ\text{C}$. <u>m</u> -carborane softened at ca. 95°C but <u>p</u> -carborane softened at $460\text{--}480^\circ\text{C}$, $n = \sim 7$

Carboranyl polymers linked by siloxanyl groups are discussed in Section 4.3.2c and carboranyl polymers without carbon side groups are discussed in Section 4.3.1.

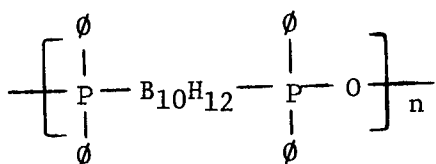
(e) Miscellaneous B-, B-N-, B-P-, Ge-, Si-
containing Polymers

The polymers covered in this section include many boron-nitrogen containing polymers, decaboranyl polymers linked with P-O-P, P-N-P, N-C, and N-C-O atoms, a silicon phthalocyanine-siloxane polymer, germanium-sulfur containing polymers, and poly(phosphinoboranes).

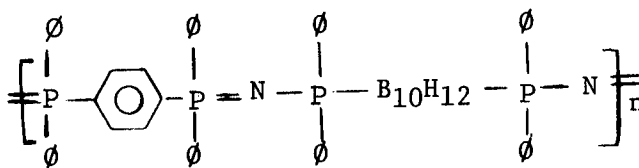
An immense effort has been made in the preparation of boron-nitrogen containing polymers [83-88]. The impetus for this effort originated in the hope that boron-nitrogen polymers would provide high temperature polymers for aerospace application. This hope in turn was based on the high B-N bond energy (106.5 kcal/mol) and that the B-N bond is isoelectronic with the C-C bond. Several major problems have been associated with the development of high performance B-N polymers. First, many B-N or B-O containing polymers display hydrolytic instability. Second, the preparation of several classes of B-N polymers (borazynes and borazenes) is hampered by the great propensity for cyclic oligomerization (See also Section 4.1.2). Third, Most materials in this class exhibited poor thermal stability, low molecular weight, and are infusible. Attempts to circumvent the hydrolytic problem usually involved designing polymers with four coordinate instead of three coordinate boron atoms or by the introduction of bulky groups near the main chain. The cyclization problem was largely resolved by introduction of other heteroatoms and by linking of boron-nitrogen rings. As a general consideration there is no strong indication that boron-nitrogen polymers with carbon groups will be thermally superior to the best organic polymers.

Some of the more interesting representative B-N containing polymers are shown in Table VI. Other B-N polymers can be found in Sections 4.1.4 and 4.3.1.

Several attractive decaboranyl polymers joined through P-O-P or P-N-P linkages were developed and found useful as binders in asbestos(chrysotile)-reinforced composites [89].



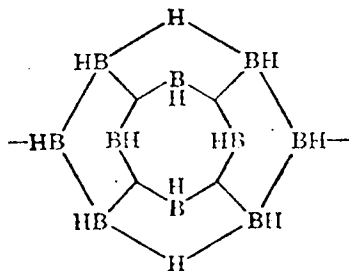
(VI)



(VII)

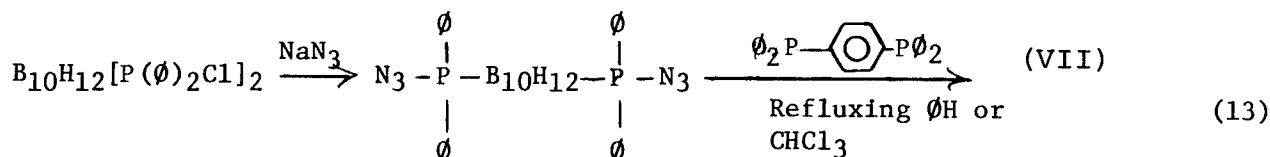
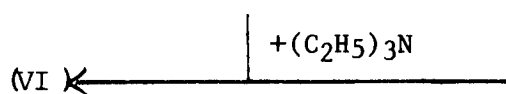
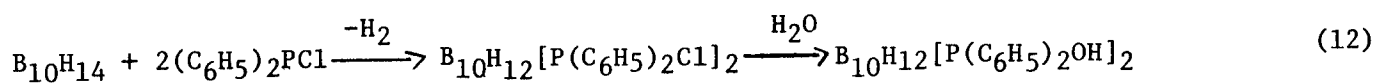
[Same as (V) in Section 5.5.3e]

where $B_{10}H_{12}$ =
(decaboranyl)



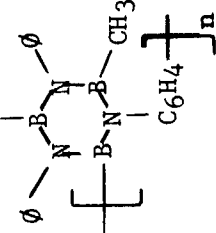
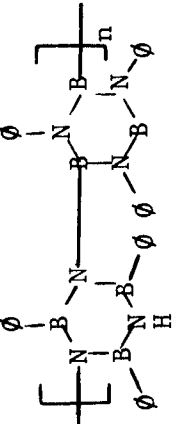
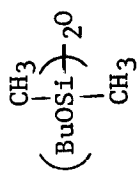
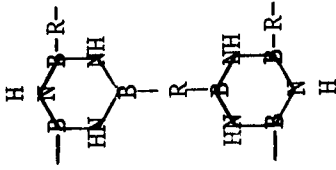
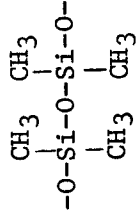
Retention of composite physical properties after air aging at 800-900°F (427-482°C) **for long periods** (i.e. 1000 hours) was outstanding [89] (also see Section 5.5.3e).

Polymers (VI) and (VII) were prepared as shown in Equations (12) and (13) [90].



Polymer (VI) had a molecular weight of about 27,000 and evolved hydrogen starting at 270° to give a crosslinked (via B-B links) polymer. Polymer (VII) starts to soften at >340°C also accompanied by loss of hydrogen and crosslinking. Polymers (VI) and (VII) were compression molded to afford asbestos-reinforced composites which showed (Figure 2) very good retention of flexural strength and flexural modulus after isothermal aging at 800°F (427°C). Composites of (VII) containing 60% chrysotile retained 97.4% and 91.6% of original weight after 200 and 600 hours, respectively, at 850°F (454°C).

TABLE VI
BORON-NITROGEN CONTAINING POLYMERS [83,86] (a)

Example	Polymer Derivation	Polymer Structure	Remarks
1	β -trimethyl-N-triphenylborazole, heat in sealed tubes at 450- 480°C/24 hrs.		Insol., infusible; in N ₂ wt. loss starts >700°C, in air wt. loss starts ca. 500°C; not hydrolyzed in H ₂ O.
2	Bulk condensation of β -triphenyl- and N-triphenylborazines		Retains 76% of wt. to 900°C (argon); hydrolyzed in boiling H ₂ O.
3	Borazole + $\text{CH}_3\overset{\text{O}}{\underset{\uparrow}{\text{P}}}(\text{OBu})_2$ or 	 R = $-\overset{\text{O}}{\underset{\uparrow}{\text{P}}}-\text{O}-\text{CH}_3$, 	M.p. >300°C, infusible

(a) And references disclosed therein.

TABLE VI (Contd.)

BORON-NITROGEN CONTAINING POLYMERS [83,86] (a)

Example	Polymer Derivation	Polymer Structure	Remarks
4	Tetrakis(dimethylamino)diboron + NH ₃		Crystalline, no melting to 500°C; at ca. 500°C crosslinks and evolves dimethylamine
5	 + BR ₃ (xylene reflux) R = alkyl		Elastomers for R = C ₂ H ₅ , R' = H; mol. wt. = 6,000 to 12,000; stable to air and boiling H ₂ O, hydrolyzed slowly by boiling alkali and rapidly by boiling HCl.
6	 + ØBCl ₂ + heat R = Ø, CH ₃		Claimed to be useful as coatings, laminating and molding resins; ØH evolved at 500°C (N ₂) when R = Ø.

(a) And references disclosed therein.

TABLE VI (Contd.)
BORON-NITROGEN CONTAINING POLYMERS [83,86] (a)

Example	Polymer Derivation	Polymer Structure	Remarks
7(b)	$ \begin{array}{c} (\text{HO})_2\text{B}-\text{C}_6\text{H}_4-\text{B}(\text{OH})_2 + \\ (\text{HO}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2)_2\text{N}-\text{CH}_2\text{CH}_2-\text{N}-(\underset{\text{CH}_3}{\text{CH}_2}\text{CH}-\text{OH})_2 \end{array} $		Turned sl. brown after 5 hrs. at 300°C and was unchanged after boiling in H ₂ O 4 hrs.

(a) And references disclosed therein.

(b) See Section 4.3.1, Table I, Ex. 3 for a non-methylated analog.

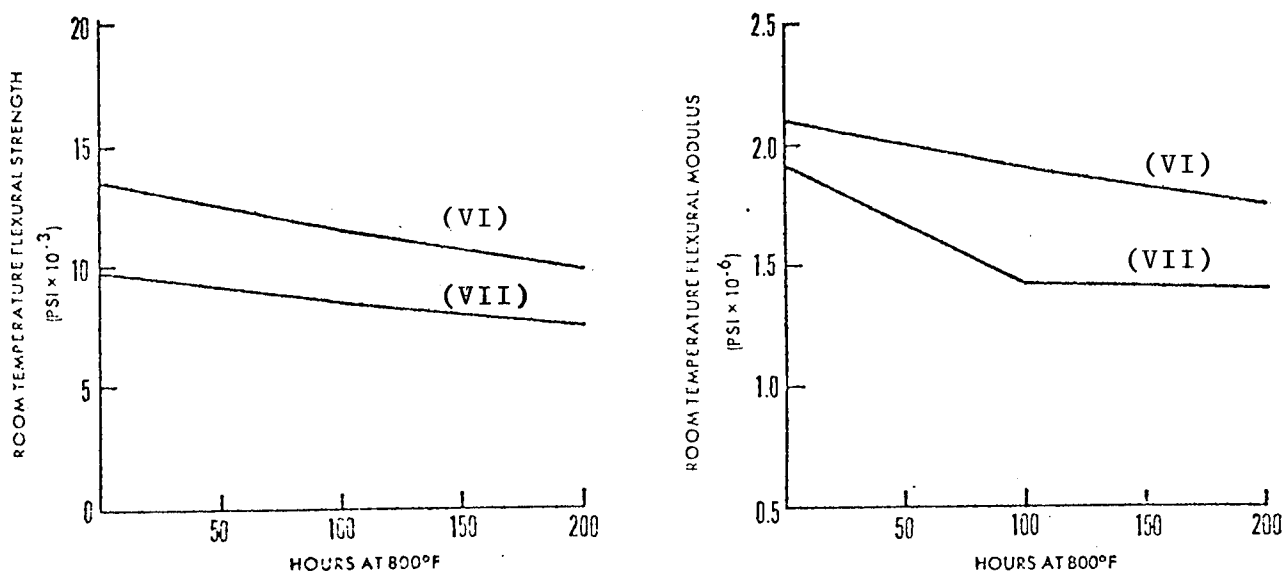
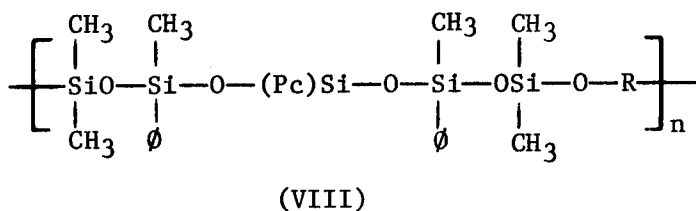
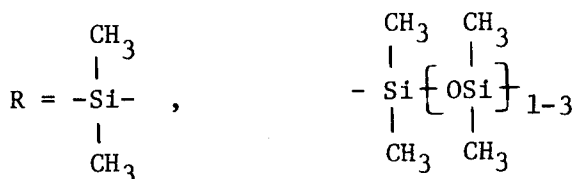
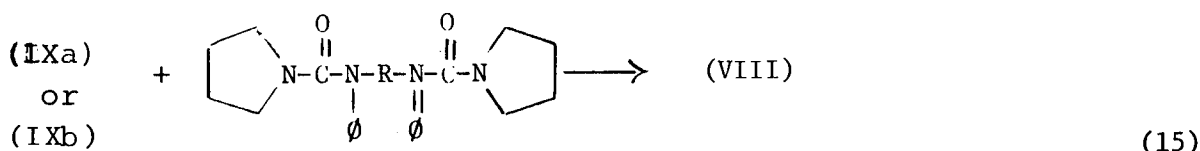
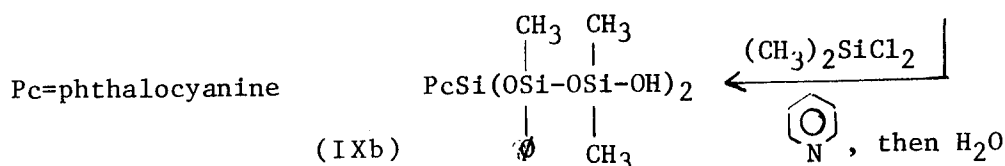
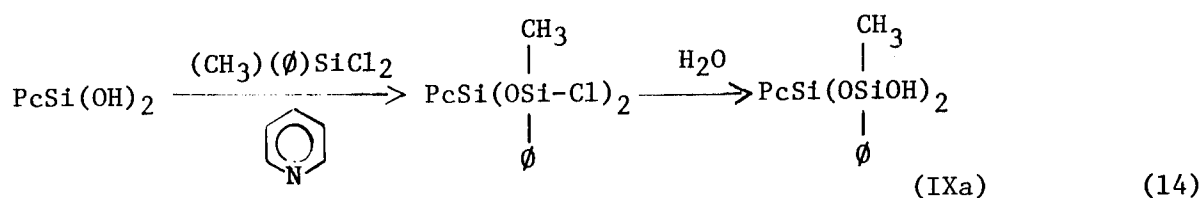


Figure 2. Effect of Heat Aging on Properties of Poly(decaboranyl-phosphorus linked) Composites [89].

The composites derived from polymers (VI) and (VII), despite some very attractive properties, had several major limitations (see Section 5.5.3e) and did not merit continued investigation.

A poly(phthalocyanine-siloxane) has been discussed in Section 4.3.1. This polymer had no carbon side groups or flexibilizing links to impart desirable solubility or processing properties. An attempt to overcome these deficiencies was made recently [41]. Polymer (VIII) was prepared by the bis(ureido)silane (or siloxane)-silanol condensation (see Sections 4.3.2c and 5.2.2) as shown in Equations (14), (15).







The phthalocyanine-siloxane polymers (VIII) have the potential for processing. They were soluble in organic solvents, had relatively low melting or softening points (65-100°C), and approximate molecular weights of 10,000 (degree of polymerization = 11-14) [41]. Thermal stability was not reported. However, initial DTA and TGA studies indicate they are at least as good as the poly(siloxanes) [91]. The solubility of polymer (VIII) is in contrast to the polymers synthesized from diols and dicarboxylic acids and PcSiCl_2 or PcSi(OH)_2 [92].

Other polymers in this section are shown in Table VII.

TABLE VII

MISCELLANEOUS POLYMERS WITH B, P, or Ge IN BACKBONE

Example	Polymer Derivation	Polymer Structure	Remarks
1 [93]	Dimethylphosphinoborane + (C ₂ H ₅) ₃ N	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{---P---BH}_2\text{---} \\ \\ \text{CH}_3 \end{array} \right]_n$	Mol. wt. 500-15,000, unstable at 190°C for several hrs.; m.p. 170- 172°C at mol. wt. = 6,014.
2 [94]	H ₃ B·RHP-R'-PHR·BH ₃ R = alkyl, aryl R' = alkylene, arylen Heat to 220°C	$\begin{array}{c} \text{R} \\ \\ \text{---P---R'---B---} \\ \\ \text{---} \end{array} \left[\right]_n$	For R = ϕ , R' = (CH ₂) ₄ infusible, glassy, stable at 300°C for several days and resistant to H ₂ O.
3 [95]	$\text{CH}_3\text{---}\overset{\text{O}}{\parallel}\text{CN(CH}_3)_2 + \text{B}_{10}\text{H}_{14}$	$\left[\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{---OCH---N---B}_{10}\text{H}_{12}\text{N---} \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n$	--
4 [96]	HS-R-SH + (ϕ) ₂ GeX ₂ R = (CH ₂) ₅ , -CH ₂ -  -CH ₂ -  -CH ₂ - X = halogen	$\left[\begin{array}{c} \phi \\ \\ \text{---Ge---S---R---S---} \\ \\ \phi \end{array} \right]_n$	For R = alkylene n = 43, soluble plastic For R = arylen n = 60, sl. sol. viscous liquid.

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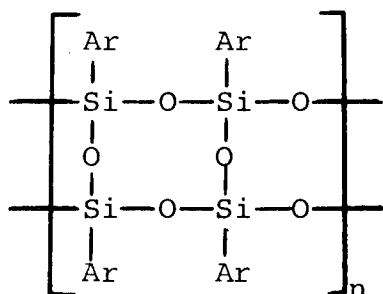
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5.0 CRITICAL REVIEW CANDIDATES

5.1 Poly(arylsilsesquioxanes)

5.1.1 Introduction

This class of polymers, having the empirical formula $[(\text{ArSiO}_{1.5})_2]_n$, Ar = aryl] are thought to be best represented by structure (I).



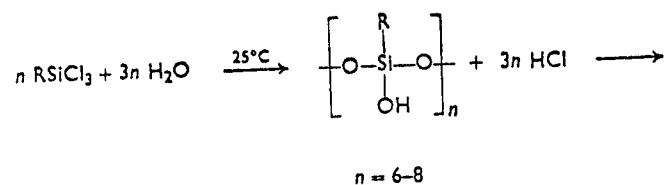
(I)

Poly(arylsilsesquioxanes), or ladder siloxanes, have been the subject of intense interest since their discovery in 1960 and form the basis of two excellent reviews [1,2]. Recent reviews [3, 4] deal more intimately with the physical properties of these materials, as they relate to application as matrix resins for the fabrication of composites.

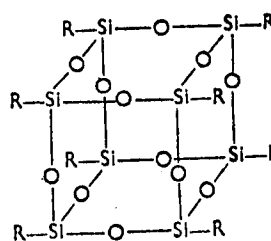
Those factors which make poly(arylsilsesquioxanes) attractive as a candidate system for this study include high molecular weight, excellent oxidative stability, resistance to hydrolysis (acidic or neutral conditons) and reasonable cost of synthesis.

5.1.2 Method of Preparation

Hydrolysis of alkyl or aryl substituted trialkoxy silanes was shown to yield low molecular weight oligomers (II) similar to those obtained from the hydrolytic condensation of alkyl substituted trichlorosilanes [5, 6]. Further investigation demonstrated that these oligomers possess a cage-like structure [7, 8] as shown in Equation (1).



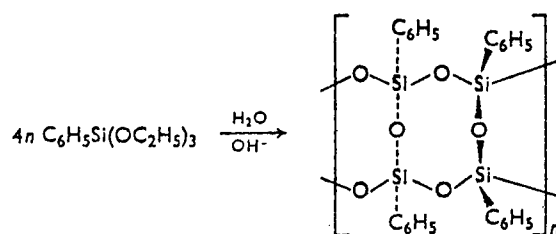
R = Ar and alkyl



(1)

(II)

Hydrolysis of phenyltriethoxy silane in the presence of a quaternary base using methyl isobutyl ketone as the solvent system resulted in formation of a polymer claimed to possess the ladder structure (III) in Equation (2) [9].

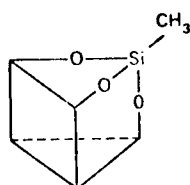


(2)

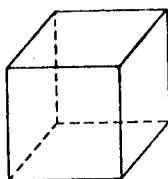
(III)

Optimization of reaction conditions for the base catalyzed equilibration of the hydrolysate obtained from either phenyltrichlorosilane or phenyltriethoxysilane (high concentration/250°C-Dowtherm) led to the isolation of soluble ladder polymers of molecular weights of the order of 10^6 [10-13a].

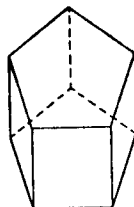
The same reaction carried out in dilute solution resulted in formation of cage-like structures, (IV), (V), (VI), (VII), and (VIII). which are thought to be readily converted to ladder polymers (Equation 3) [13b-17] via prepolymer (X)



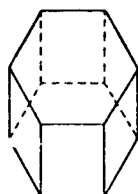
(IV)



(V)



(VI)

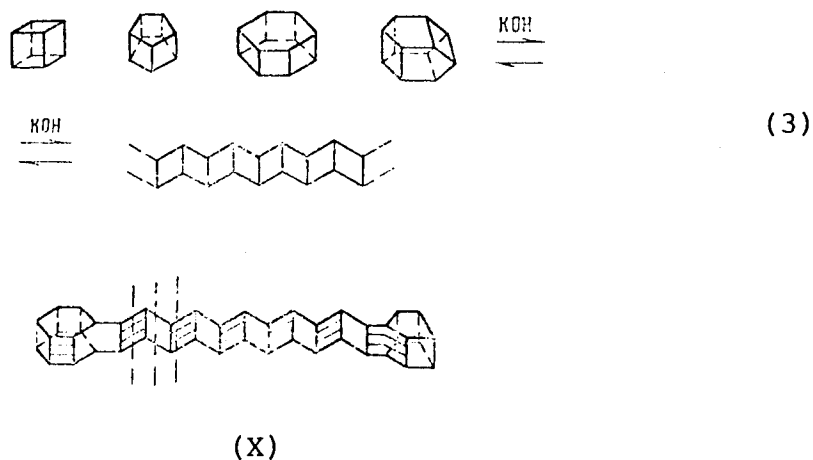


(VII)

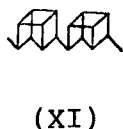


(VIII)

N.B. The eight-membered ring segments are depicted by squares, but the presence of oxygen between each pair of silicon atoms is to be assumed, as is an alkyl or aryl substituent at each corner silicon atom (as suggested by the $\text{CH}_3\text{-Si}$ in the first structure) [13a].



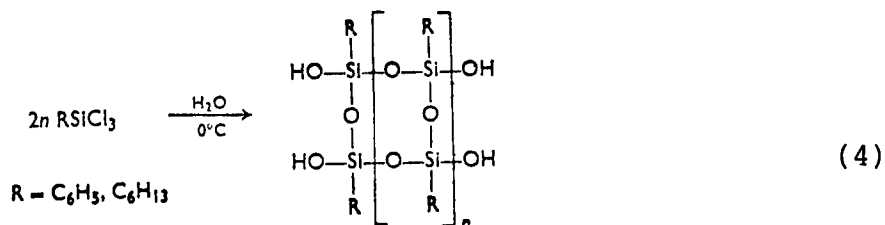
Considerable effort has been put forward in support of the ladder type structure [18, 19, 20], but the matter is still not fully resolved. Arguments in support of the ladder configuration based upon equilibrium effects at high concentration can also be interpreted in terms of a random array of polycyclic cages (XI) [21, 22]:



The fact that no silanol functionality is detected, coupled with the physical properties exhibited by this material, leads to the inference that cyclization of chain ends has occurred. This can be interpreted as a doubling back of chain ends to effect a type of internal recyclization that results in a disordered structure.

Regardless of their true structure, poly(arylsil-sesquioxanes) possess unique and potentially useful characteristics [23] and considerable attention has centered around their use as heat and corrosive-resistant laminates for use in electrical insulation, coating exhaust pipes and ovens [24, 25], and as molding compositions for prepreg carbon filled plastics [26].

Hydroxy terminated poly(phenylsilsesquioxanes) (XII)



(XII)

prepared by the low temperature hydrolysis of trichlorosilanes [21,28] (Equation 4) will copolymerize with difunctional silane monomers to yield copolymers possessing intrinsic viscosities of 0.17-0.29 dl/g [28-30]. In addition, (XII) ($n = 280$) can undergo further self-condensation to yield higher molecular weight analogs exhibiting intrinsic viscosities of 0.56 dl/g [25]. Extremely high molecular weight (intrinsic viscosity = 3.1) block copolymers can be prepared directly from low molecular weight organopolysiloxanes via reaction with either trifunctional arylsilane hydrolyzate or arylsilsesquioxane polymers under alkaline rearrangement/condensation conditions [27].

For a treatment of those conditions of synthesis which have been shown to affect the resulting structure of poly(silsesquioxanes), the reader is advised to consult the references indicated [31-36].

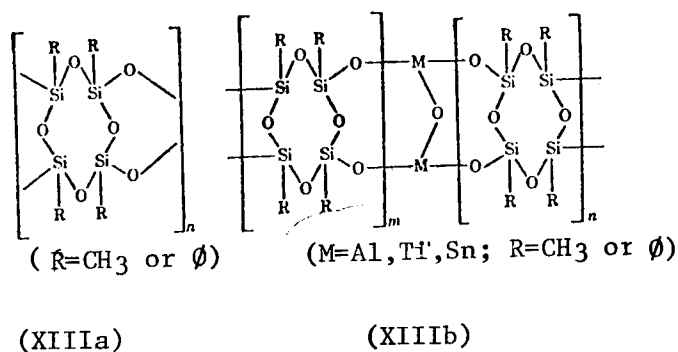
5.1.3 Properties

Poly(phenylsilsesquioxanes), prepared by elevated temperature equilibration (250°C) of a concentrated solution of phenylsilsesquioxane prepolymers, were more resistant to hydrolysis than corresponding poly(phenylsiloxanes) [18]. Thermal aging in steam is comparable to that observed in air and tensile strengths almost twice those recorded for analogous siloxanes have been observed.

Analysis of the TGA (air) curve for poly(phenylsil-sesquioxane) indicates a break at 525°C. Thin film strips were unaffected by exposure for short periods at temperatures of 650°C or instantaneous exposure to red heat [18]. Heating to 900°C did not cause degradation of the polymer backbone but weight loss did occur due to oxidation of the phenyl groups [28].

As already indicated, polymers of very high molecular weights can be prepared while maintaining good solvent solubility. This allows for the casting of tough transparent films exhibiting Tg values of the order of 300°C [12]. In one instance a Tg value of 400°C was observed [37].

Additional thermal stability is claimed via the inclusion of stabilizers such as CuSiO_3 [38], although the effect appears to be most pronounced with poly(alkylsil-sesquioxanes) (XII). Similar results were obtained when salts of Al, Ti, and Sn were reacted with poly(alkyl or aryl sesquioxanes), leading to incorporation of the metal as shown in (XIIIa and b) [39,40,41].



It is theorized [42] that introduction of the metal leads to an increase in the polarity of the Si-R bond. If thermal degradation indeed proceeds via nucleophilic attack of oxygen on either the Si-R or Si-O bond, thermal stability is expected to increase when R = alkyl and to decrease when R = aryl, which corresponds to the observed facts.

Further investigation into the mechanism of thermal degradation of these materials has shown [43,44,45] that the oxidation rate is dependent upon the oxidative susceptibility

of the organic substituents and the tendency of the siloxane skeleton to undergo rearrangement. In addition, the relative frequency of depolymerization increases as the alkyl to phenyl ratio increases. Degradation rate was also found to depend upon the presence of ionic centers, defects, and structure regularity [44].

Several peculiar features of this polymer have been established and have been related to chemical structure [46,47]. The stress-strain curves (Figure 1) provide an estimate of strength of system under study.

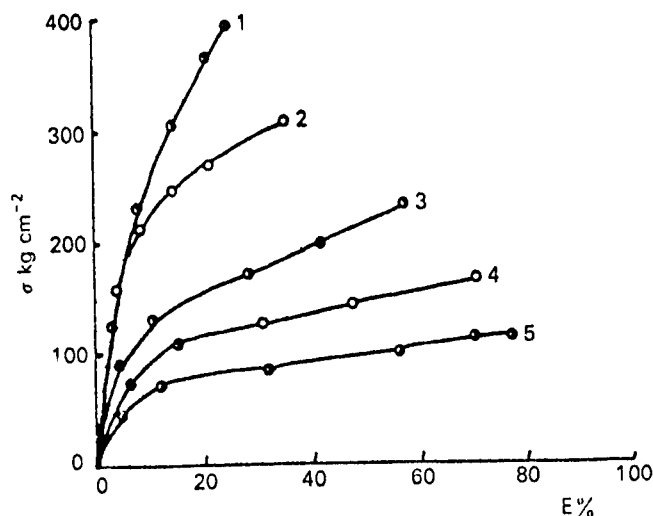


Figure 1. Stress-strain plots for organosilicon ladder polymers at $T = 100^{\circ}\text{C}$. (1) polyphenylsilsesquioxane, $[\eta] = 2.8$; (2) polyphenylisobutylsilsesquioxane $[\eta] = 1.9$, 66% phenyl groups; (3) polyphenylisoamylsilsesquioxane $[\eta] = 2.2$, 75% phenyl groups; (4) polyphenylisobutylsilsesquioxane $[\eta] = 1.9$, 75% phenyl groups; (5) polyphenylisobutylsilsesquioxane $[\eta] = 2.5$, 75% phenyl groups. [46]

As another example (Figure 2), a study was made of the relative ultimate elongation for poly(phenylisobutylsilsesquioxane).

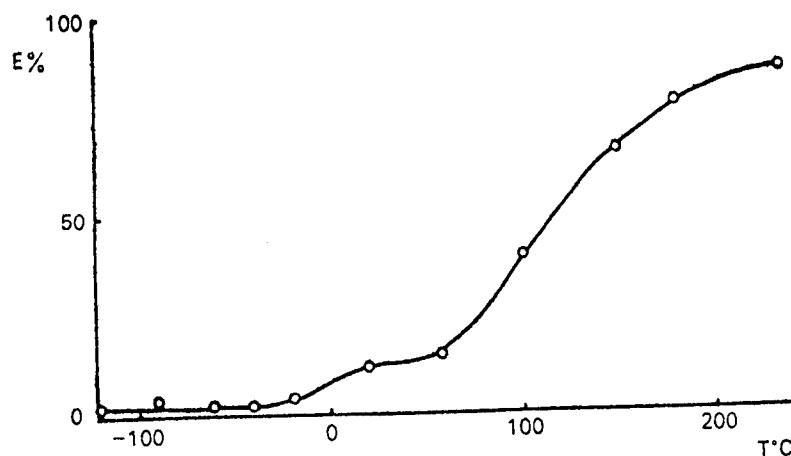


Figure 2. Temperature dependence of ultimate elongation of poly(phenylisobutylsilsesquioxane) [46]

This curve can be arbitrarily divided into three regions characterized by various degrees of tensile deformation. At temperatures ranging from -100 to -20°C , deformation is equal to 3-5% and is completely reversible, i.e. elastic. Within the temperature range between -20 and $+60^{\circ}\text{C}$ the deformation limit amounts to 20%; with the load removed, this deformation is completely or partially (not less than by half) reversible. The third temperature range (over 60°C) is characterized by a sharply increased deformation limit (up to 100%) which is also, to a great extent, reversible. A one-hour annealing of samples at 140°C contributes to a greater percentage of reversible deformation; after annealing, the total reversible deformation is about 75% of the initial deformation. The observed effects may be illustrated by measuring the shrinkage of preoriented films of organo-silicon ladder polymers upon subsequent heating (Figure 3).

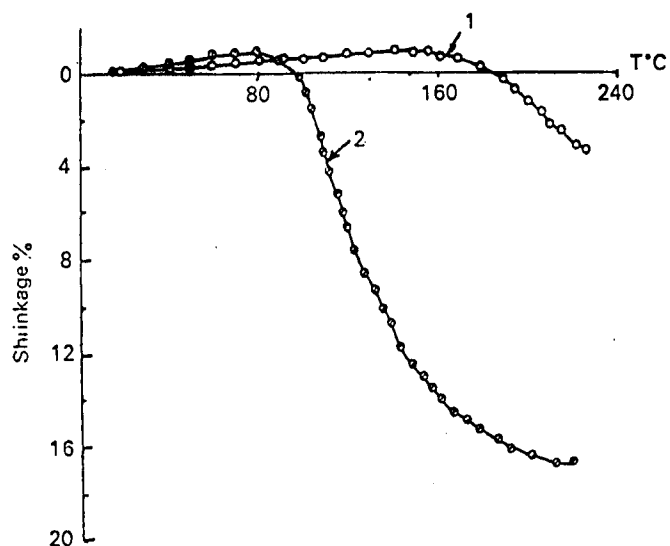


Figure 3. The shrinkage kinetics of pre-oriented films of (1) poly(phenylsilsesquioxane) and (2) poly(phenylisobutylsilsesquioxane) upon heating. [47]

The dynamic Young's modulus (E') and the tangent of the mechanical loss angle ($\tan \sigma$) were measured over a wide temperature range. The temperature dependences of E' for various polymers are presented in Figure 4. As can be seen,

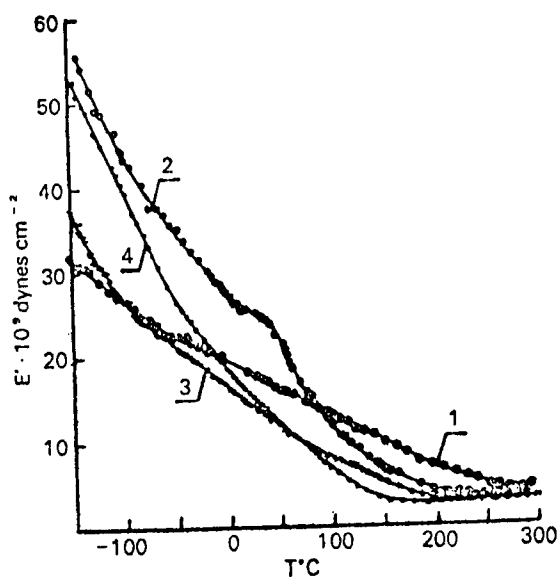


Figure 4. E' vs temperature plots for (1) poly(phenylsilsesquioxane), (2) poly(phenylisobutylsilsesquioxane), (3) poly(phenylisobutylsilsesquioxane), (4) and poly(phenyl-n-hexylsilsesquioxane) with the phenyl-alkyl group ratio 3:1. [47]

with the temperature rise from -150 to $+300^{\circ}\text{C}$, the E' -value goes from $3\text{--}5 \cdot 10^{10}$ down to $5 \cdot 10^9$ dynes cm^{-2} . It is noteworthy that the absolute E' -values and the temperature coefficients of their variations over the temperature range from -150 to 0°C are comparable with those for several organic polymer systems, e.g., polystyrene or polyethylene terephthalate. An investigation of the temperature dependence of $\text{tg } \sigma$ has revealed that the two regions of decreasing E' -values correspond to the two wide regions of relaxation processes which [37] have arbitrarily called the regions of low- and high-temperature transitions. A typical averaged temperature dependence of $\text{tg } \delta$ is shown in Figure 5.

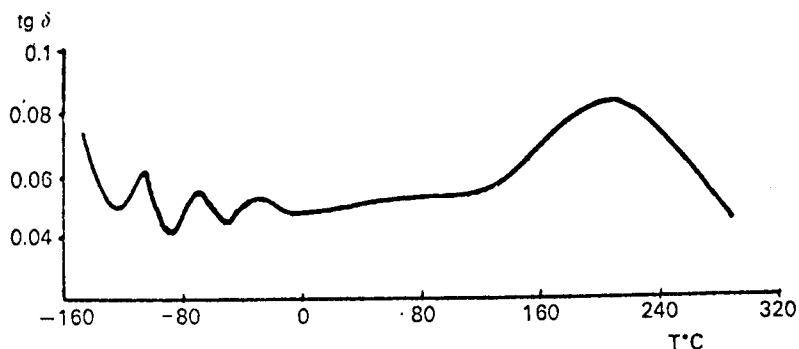


Figure 5. Typical averaged $\text{tg } \delta$ -temperature plot for organosilicon ladder polymers. [47]

An analysis of this plot shows several relaxation maxima in the low-temperature region (-145 , -100 , -70 , and -30°C). Here the $\text{tg } \delta$ values are at maximum within $0.06\text{--}0.1$ and just correspond to those typically observed on secondary transitions in organic polymers. Neither the position of the relaxation maxima on the temperature scale nor their intensity is dependent on the type and relationship of the organic radicals around the main chain. The fact that the character of the low-temperature transitions is independent of the chemical structure of organosilicon ladder polymers, each of which contains a particular number of phenyl groups, suggests that they are related, directly or indirectly, to the appearance of new degrees of phenyl group motion at elevated temperatures. Torsional vibrations of side phenyl groups are known to develop in some polymers over temperatures from -200 to -100°C . One can assume by analogy that over

this temperature range the phenyl groups in organo-silicon ladder polymers acquire an additional freedom of torsional vibration due to weaker interaction therein upon heating. This, in turn, may initiate local motions of the main chain which, rigid as it is, is in principle capable of slight torsion around its longitudinal axis.

Tensile strengths for poly(phenylsilsesquioxane) were measured and found to be 3400-6000 psi [18,9,15] with elongations ranging from 3-16%. At 250°C, the polymer possessed a tensile strength of 1090 psi and an elongation of 12%, indicating a $T_g > 250^\circ\text{C}$.

5.1.4 Summary and Recommendations

On the basis of the published data, poly(arylsilsesquioxanes) would appear to be ideal candidates for preparing advanced composite materials. Molecular weights in excess of one million have been achieved while maintaining good solvent solubility and processability, and thermal and chemical resistance is claimed to be excellent. The logical question is then -- if these materials are truly superior, why haven't they been commercialized?

Part of the answer is to be found in the controversy surrounding the nature of the polymer structure. There is indeed serious doubt regarding the proposed ladder structure, and many of the extrapolated claims which were based upon this unique configuration have been substantially modified. Another part of the answer lies in the inability to prepare polymers possessing consistent physical and chemical properties. This difficulty stems from variables associated with the synthesis of these materials.

The preparation of poly(arylsilsesquioxanes) involves a three step reaction:

- (1) Generation and isolation of the aryl-trihalosilane hydrolysate.
- (2) Thermal conversion of the hydrolysate to prepolymer (not isolated).
- (3) High temperature (250°C) conversion of prepolymer to polymer.

The first stage is rather straight forward and proceeds with an efficiency of approximately 50%. Thermal conversion to prepolymer is a complex reaction and leads to a diverse mixture of products (cage monomers, cage and linear polymers). The distribution of these products is controlled by reaction temperature, solvent, and catalyst and significantly affects the nature of the polymer formed during the high temperature conversion step. Equally important in achieving a good yield (70%) of polymer is the concentration at which the conversion is carried out. Concentrations just below the gel point (80-90%) have been found best but gel formation is difficult to avoid. An excellent treatment of the effect of reaction condition upon polymer structure has been prepared [3].

It would therefore appear that continued optimization of reaction conditions must be carried out before a meaningful candidate can be selected. Improved control of prepolymer product distribution may lead to interesting block copolymer systems. The per pound cost of polymer derived from phenyltrichlorosilane (\$2.36/lb) is estimated to be approximately \$25. This is based on achieving a 40% overall conversion to polymer.

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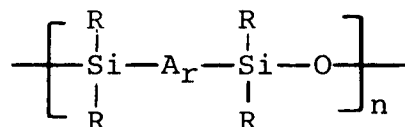
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5.2 Poly(silylarylene-siloxanes)

This class of polymers was recently the subject of an excellent review [1]. The materials can be classified into three groups:

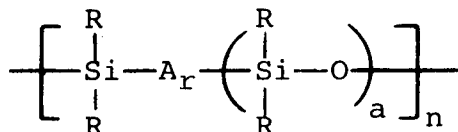
Alternating poly(silylarylene-siloxanes)



(I)

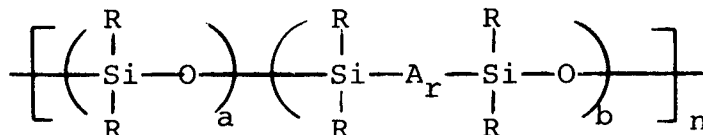
R = alkyl or aryl
A_r = arylene

Siloxane modified poly(silylarylenes)



(II)

Silylarylene-siloxane block polymers



(III)

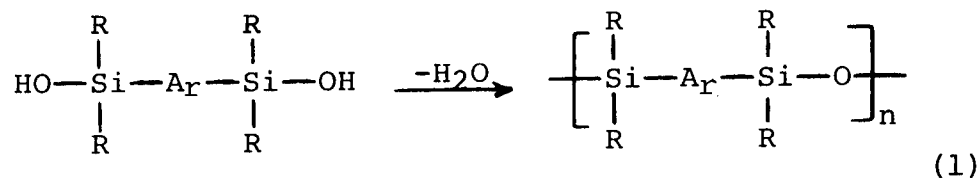
5.2.1 Introduction

Conventional poly(siloxanes) suffer from two major deficiencies with regard to their use as composite materials; hydrolytic instability and thermal depolymerization at high temperature (>300°C). Introduction of the silylarylene moiety onto the siloxane backbone does much to offset these shortcomings. The Si-C bond, although of lower bond energy than the Si-O bond [2] is much more resistant to cleavage under hydrolysis [3]. Moreover, the aromatic character of the silylarylene unit serves to prevent thermal unzipping to low molecular weight cyclic products [4]. This can be readily seen by comparing the thermal degradation temperature of poly(dimethylsiloxane) (350°C) with that of poly(tetramethyl-p-silylphenylene siloxane) (450°C) [5].

5.2.2 Methods of Preparation

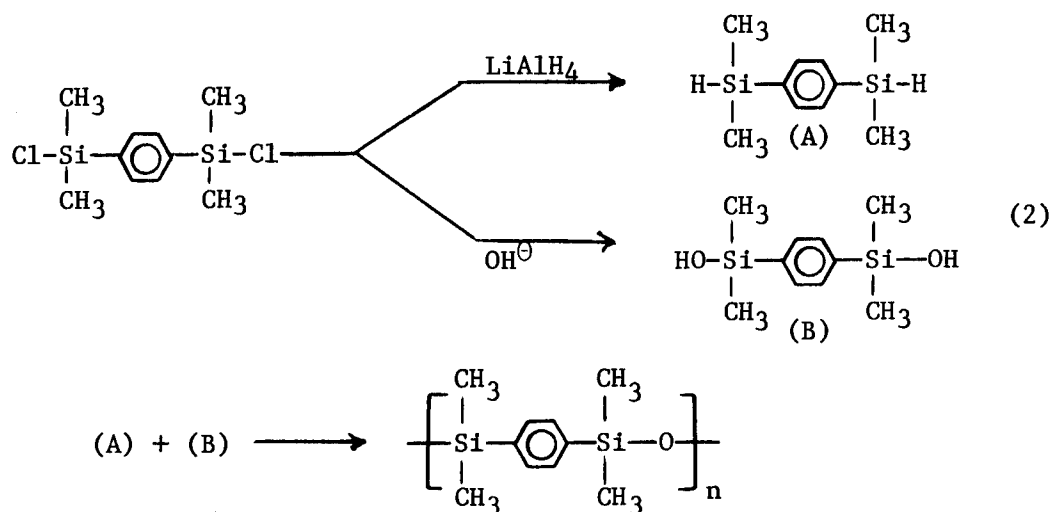
Alternating poly(silylarylene-siloxanes)

The most direct method of preparing this class of polymers involves the self condensation of p-bis(dialkyl or diaryl)hydroxysilylarylenes (Equation 1).

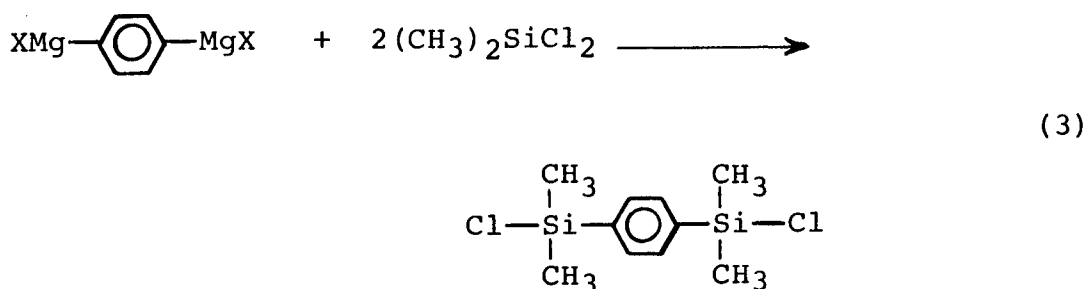


This reaction is carried out under inert atmosphere and is catalyzed by the presence of alkali metal hydroxides [6]. Lower reaction temperatures can be realized by the use of the appropriate catalyst such as n-hexylamine-2-ethylhexanoate [7] or trimethylsilylacetate [8].

A somewhat more elaborate condensation makes use of the appropriate silane and hydroxysilylarylene (Equation 2) [9].

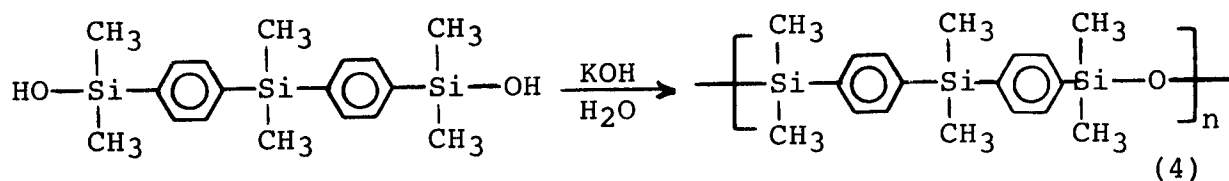


The above reaction makes use of the most common means of preparing *p*-bis-dialkyl or diaryl hydroxysilarylenes; i.e. the hydrolysis of the corresponding dihalosilane. This intermediate in turn is prepared via use of organometallic reagents as outlined in Equation (3) [10, 11].

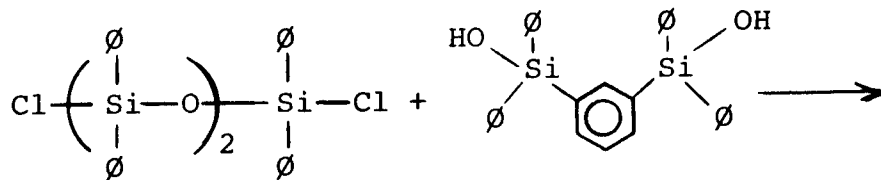
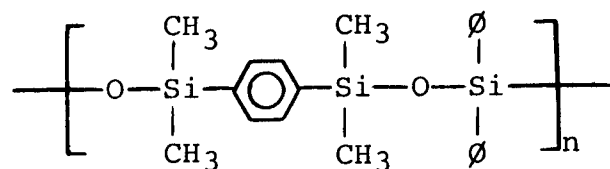
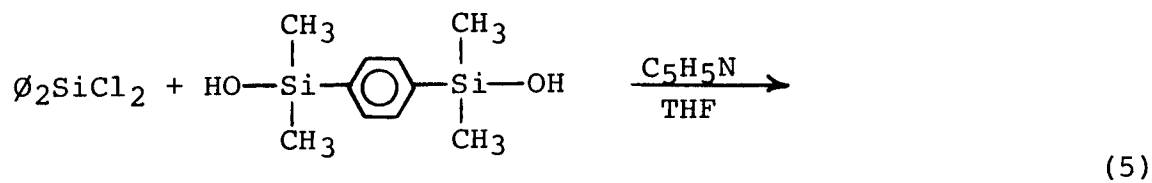


Siloxane-modified poly(silylarylenes)

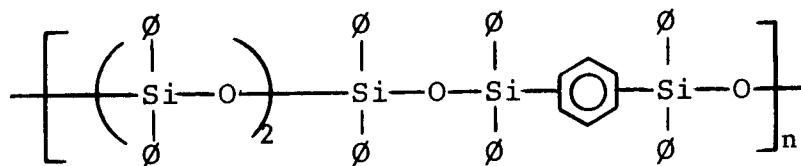
a. Self-condensation [12]



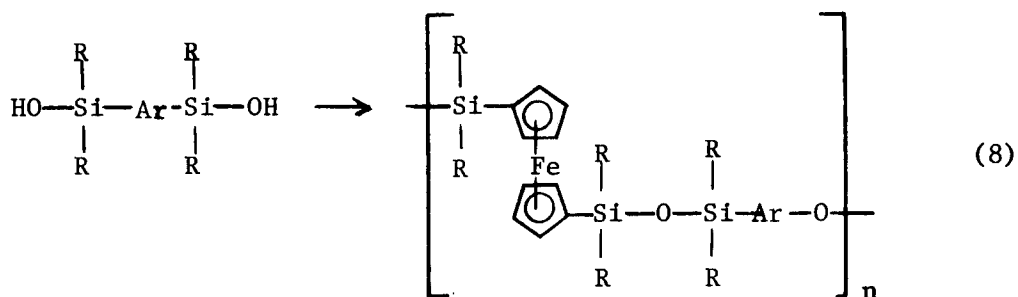
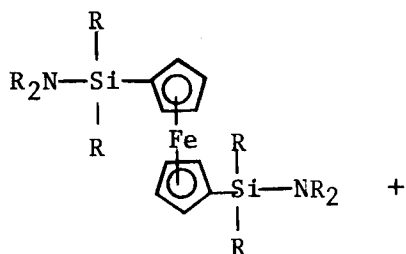
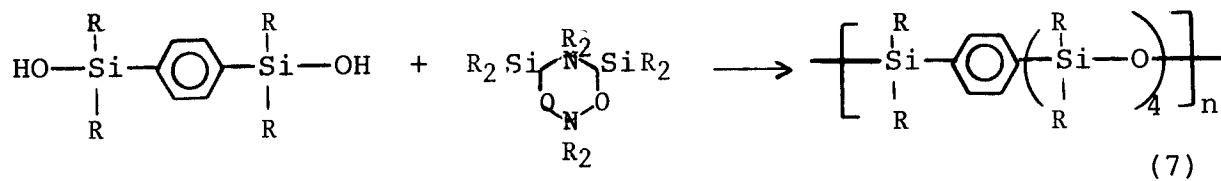
b. Condensation with dihalosilanes
(Equation 5) [13] and Equation 6)
[14].



(6)



c. Reaction with silazanes [Equation 7) [15],
and silamines (Equation 8) [16] and
Equation 9 [17].

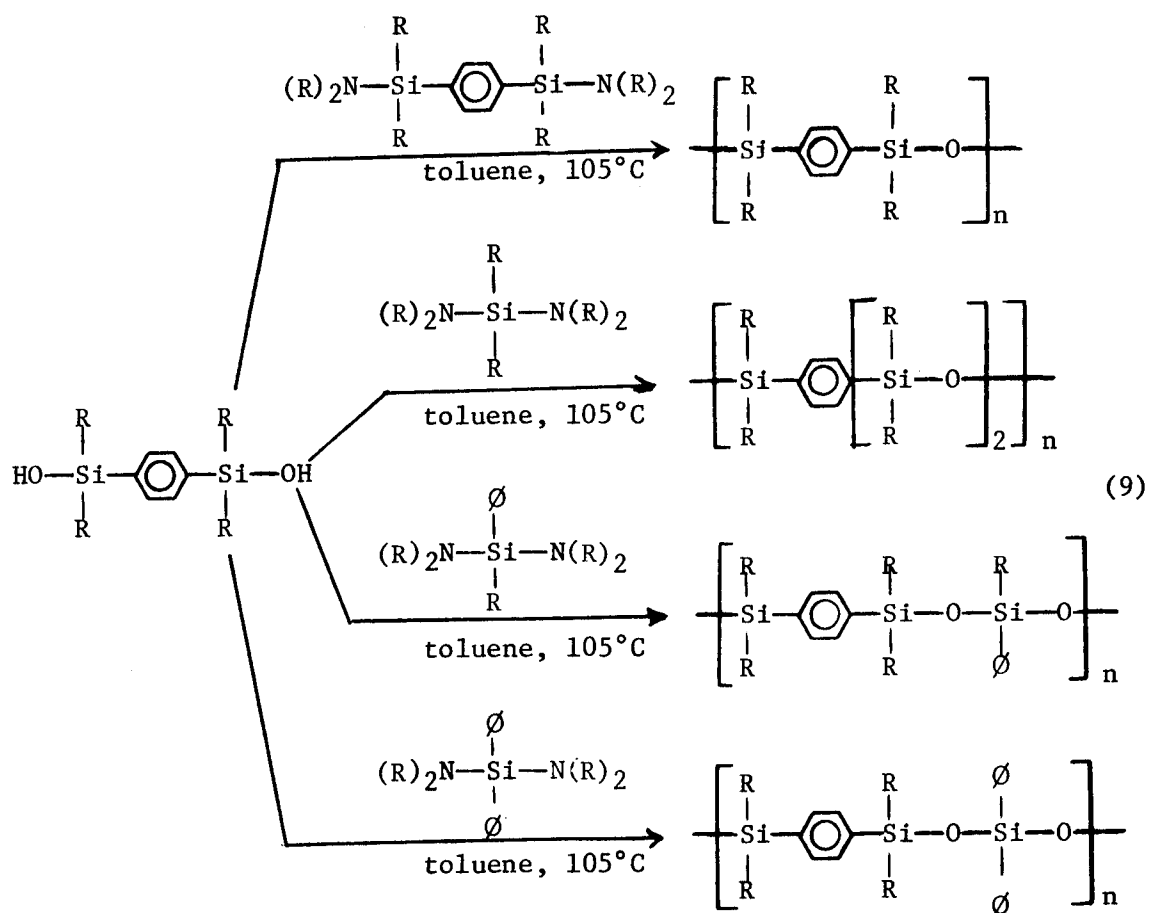


A. $\text{Ar} = -\text{Si}(\text{O}_2)-$

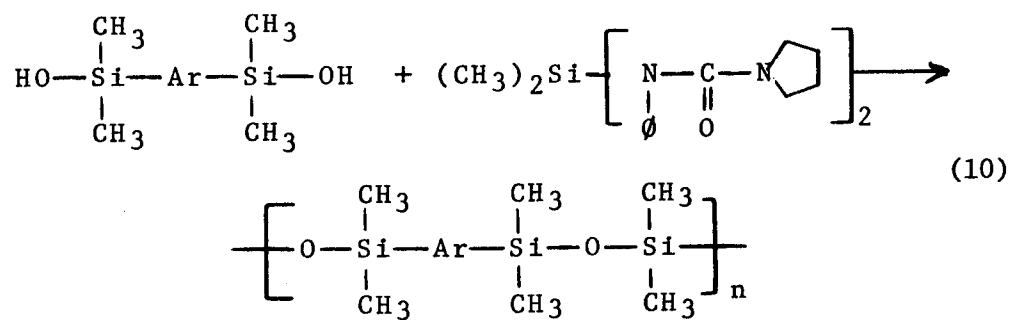
$\text{R} = \text{CH}_3$

B. $\text{Ar} = -\underset{\text{R}}{\overset{\text{R}}{\text{Si}}}-\text{C}_6\text{H}_4-\underset{\text{R}}{\overset{\text{R}}{\text{Si}}}-$

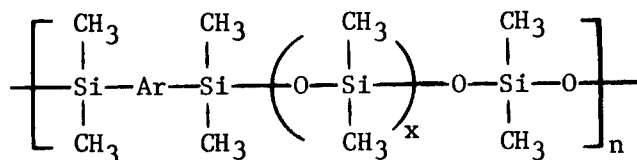
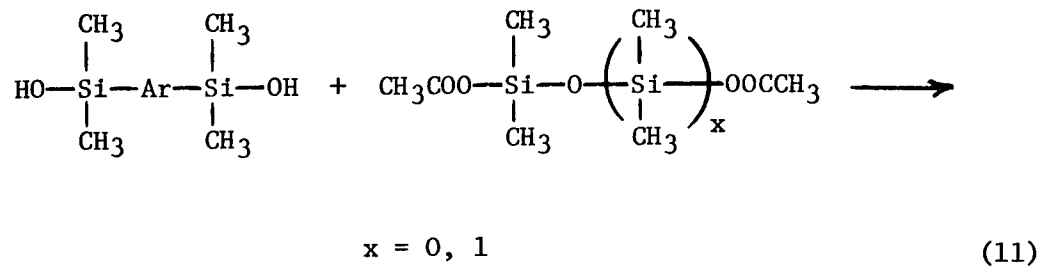
C. $\text{Ar} = -\underset{\text{R}}{\overset{\text{R}}{\text{Si}}}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\underset{\text{R}}{\overset{\text{R}}{\text{Si}}}-$



d. Reaction with bis(ureidosilanes) (Equation 10) [18,19].

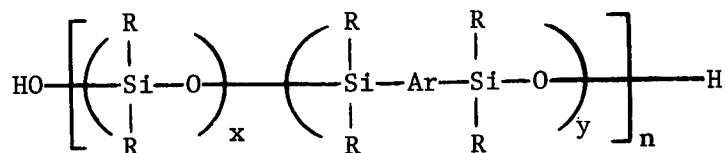
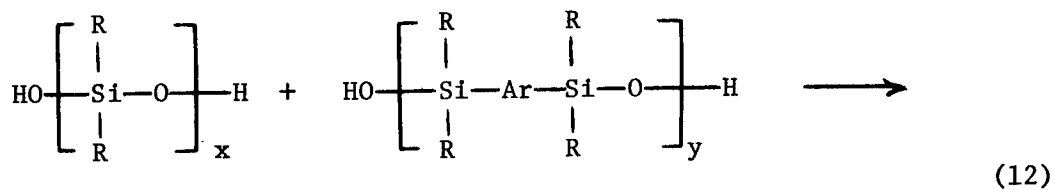


e. Silanol-acetoxysilane condensation
(Equation 11) [20].

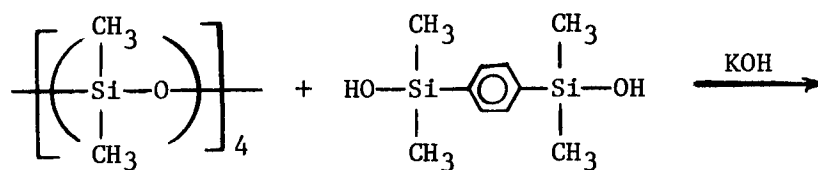


Silylarylene-siloxane block polymers [21]

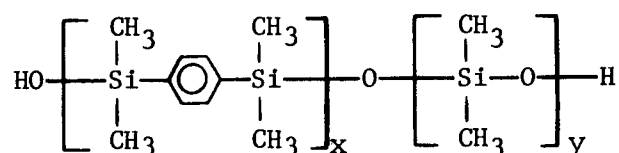
a. Condensation of hydroxy end-blocked poly-siloxanes with silylarylene-silane (Equation 12) [23].



- b. Selective copolymerization of monomers
(Equation 13) [24].



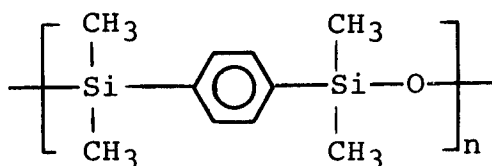
(13)



5.2.3 Properties

Alternating poly(silylarylene-siloxanes)

The simplest polymer in this class (IV) is that derived from the self-condensation of *p*-bis(dimethylhydroxy-silyl)benzene.



(IV)

When prepared via alkali metal hydroxide catalysis, the polymer can be either cast as a film or cold drawn into fibers

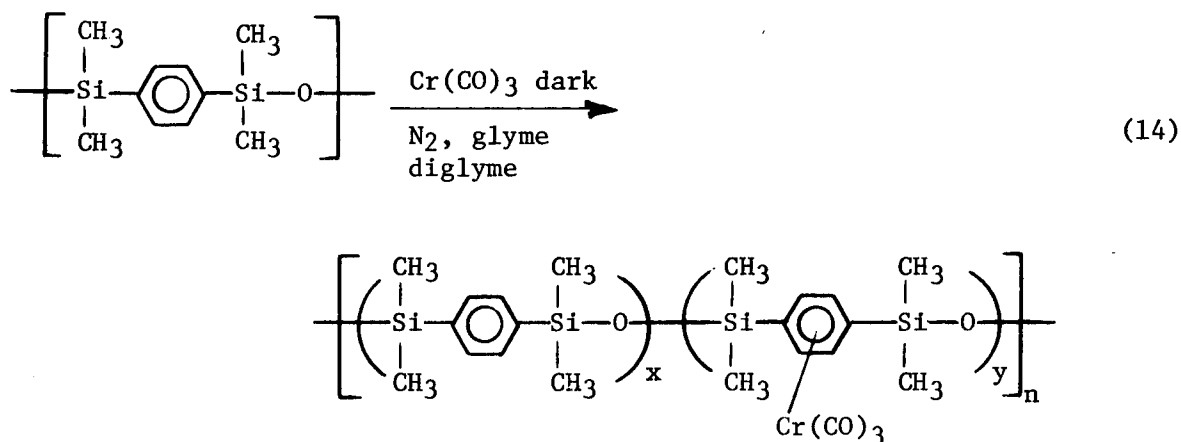
possessing the following properties [7]:

Melting temperature	125-27°C
Shrinkage (boiling water)	9%
Recovery from bending	88%
Modulus of elasticity	100,000 psi

Higher melting temperatures (148°C) can be achieved by use of n-hexylamine-2-ethylhexanoate as the catalyst [7]. The molecular weight obtained under these conditions was of the order of 250,000. The thermal stability (air) of this material was found to be appreciably higher than that of corresponding siloxanes (5% wt. loss at 225°C after 128 hours versus 20% loss for poly(dimethylsiloxane) under identical conditions).

Substitution of the 4,4'-diphenyl ether moiety for p-phenylene in this polymer system results in a further increase in resistance to thermal degradation [25]. Conversely, replacement of p-phenylene with m-phenylene clearly reduces thermal stability.

Attempts to improve the thermal stability of of arylene-siloxane polymer via metal complexation (Equation 14) resulted in chain scission yielding lower molecular weight polymers as well as diminished thermal characteristics [26].



2. Siloxane modified poly(silylarylenes)

Incorporation of siloxane units into the poly-silylarylene backbone results in the anticipated increase in flexibility. These materials can be effectively crosslinked by IR or UV radiation [14,27,28] as well as by ester exchange catalyzed by metal salts [29]. Silphenylene-siloxane polymers filled with silica and cured with metal salts have been shown

TABLE I
EFFECT OF STRUCTURE UPON T_g [15]

Polymer Structure (R = CH ₃)	η_{inh} (0.5% Solution in Toluene at 30°C)	T _g (°C)
$\left[\text{SiR}_2 - \text{C}_6\text{H}_4 - \text{O} - \text{C}_6\text{H}_4 - (\text{SiR}_2\text{O})_3 \right]_n$	2.48	-37
$\left[\text{SiR}_2 - \text{C}_6\text{H}_4 - \text{O} - \text{C}_6\text{H}_4 - (\text{SiR}_2\text{O})_4 \right]_n$	2.72 *	-52
$\left[\text{SiR}_2 - \text{C}_6\text{H}_4 - \text{O} - \text{C}_6\text{H}_4 - (\text{SiR}_2\text{O})_5 \right]_n$	3.83	-65
$\left[\text{SiR}_2 - \text{C}_6\text{H}_4 - (\text{SiR}_2\text{O})_3 \right]_n$	0.73	-62
$\left[\text{SiR}_2 - \text{C}_6\text{H}_4 - (\text{SiR}_2\text{O})_4 \right]_n$	2.77 **	-72
$\left[\text{SiR}_2 - \text{C}_6\text{H}_4 - (\text{SiR}_2\text{O})_5 \right]_n$	2.48	-80
$\left[\text{SiR}_2 - \text{C}_6\text{H}_4 - (\text{SiR}_2\text{O})_4 \right]_n$	1.60	-75
$\left[\text{SiR}(\phi) - \text{C}_6\text{H}_4 - \text{SiR}(\phi)\text{O}(\text{SiR}_2\text{O})_3 \right]_n$	0.15	--
$\left[\text{SiR}(\phi) - \text{C}_6\text{H}_4 - \text{SiR}(\phi)\text{O}(\text{SiR}_2\text{O})_3 \right]_n$	1.62	-42
$\left[\text{Si}(\phi)_2 - \text{C}_6\text{H}_4 - \text{Si}(\phi)_2 - \text{O}(\text{SiR}_2\text{O})_3 \right]_n$	0.21	--
$\left[\text{Si}(\phi)_2 - \text{C}_6\text{H}_4 - \text{Si}(\phi)_2 - \text{O}(\text{SiR}_2\text{O})_3 \right]_n$	0.66	--
* $\bar{M}_w = 905,000$		** $\bar{M}_w = 820,000$

to exhibit tensile strengths as high as 2800 psi [28]. The effect of polymer structure and composition upon physical properties can be seen in Table I and Figure 1 [15]. Clearly the 4,4'-diphenyl ether analog having the lowest siloxane content demonstrates superior thermal resistance.

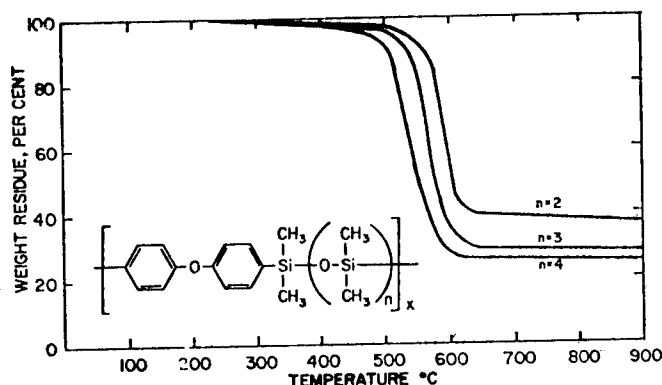
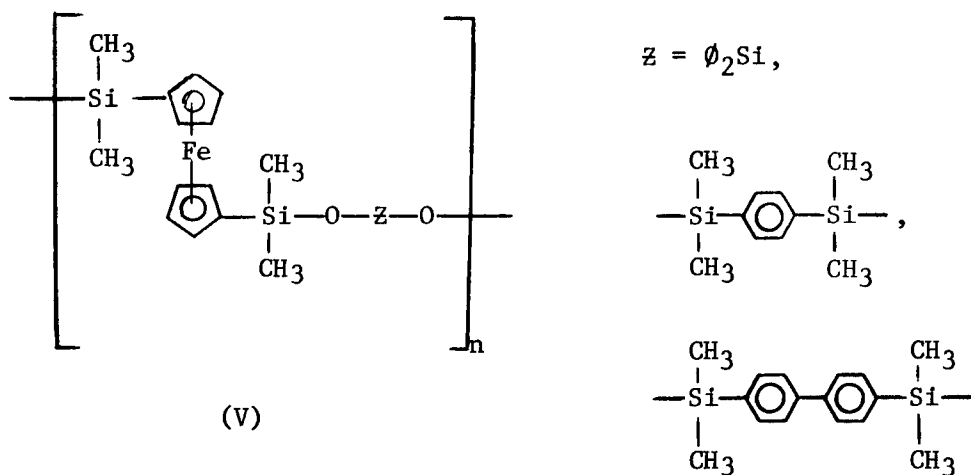


Fig. 1. Thermogravimetric analysis of polyarylenesiloxanes. Heating rate, 15°C./min.; N₂ atmosphere. [15]

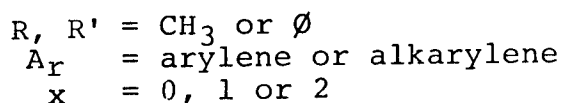
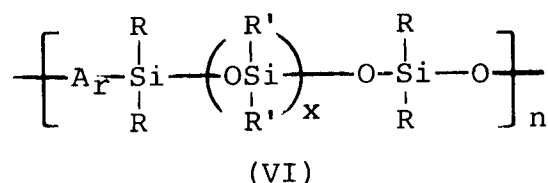
Ferrocene polymers of the type (V)



were prepared [16] and found to be more hydrolytically stable than the simpler *p*-phenylene analogs (also see Section 5.4).

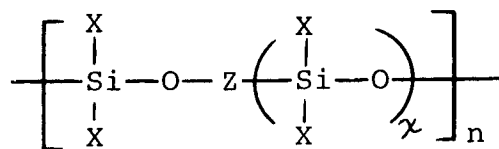
Polymers prepared by silylamine condensation techniques were found to exhibit properties presented in Table II [17].

Introduction of dimethylsiloxane units is shown to systematically decrease Tg and thermal stability. Replacing Si-CH₃ with Si-C₆H₅ increases these values while replacing the p-phenylene unit with ferrocene increases the Tg value but slightly decreases thermal stability. Further credence for the conclusion is given by the recent work by Rosenberg [20] in which polymers of the type (VI)



were prepared and evaluated. Those polymers most resistant to thermal degradation possessed the highest aromatic substitution (R=∅).

A more recent study dealing with the correlation between polymer structure and glass transition temperature for this class of polymers [30] made use of the model system (VII).



(VII)

X = alkyl
 Z = alkylene or arylene

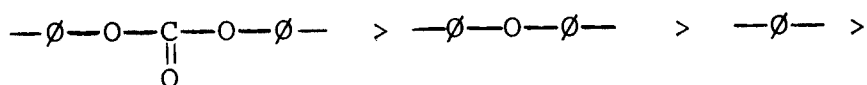
It was found that Tg values increased with the size and bulk of X. For the systems under study (X = CH₃), the nature of R increased Tg according to the following sequence:

TABLE II

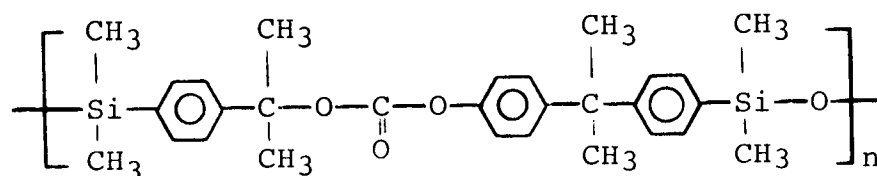
EFFECT OF STRUCTURE UPON T_g [17]

Polymer Structure (R = CH ₃)	T _g , °C ^a
$\left[\text{SiR}_2 - \text{C}_6\text{H}_4 - \text{SiR}_2\text{O} \right]_n$	-25
$\left[\text{SiR}_2 - \text{C}_6\text{H}_4 - \text{SiR}_2 - \text{OSiR}_2 - \text{O} \right]_n$	-61 (-65)
$\left[\text{SiR}_2 - \text{C}_6\text{H}_4 - \text{SiR}_2\text{O} - (\text{SiR}_2\text{O})_2 \right]_n$	-88
$\left[\text{SiR}_2 - \text{C}_6\text{H}_4 - \text{SiR}_2\text{O} - (\text{SiR}_2\text{O})_3 \right]_n$	-102
$\left[\text{SiR}_2 - \text{C}_6\text{H}_4 - \text{SiR}_2\text{O} - \text{Si}(\phi)\text{O} \right]_n$	-25 (-32)
$\left[\text{SiR}_2 - \text{C}_6\text{H}_4 - \text{SiR}_2\text{O} - \text{Si}(\phi)_2\text{O} \right]_n$	1 (-4)
$\left[\text{SiR}_2 - \text{C}_5\text{H}_4\text{FeC}_5\text{H}_4 - \text{SiR}_2\text{O} - \text{Si}(\phi)_2\text{O} \right]_n$	(37)
$\left[\text{SiR}_2 - \text{C}_5\text{H}_4\text{FeC}_5\text{H}_4 - \text{SiR}_2\text{O} - \text{SiR}_2 - \text{C}_6\text{H}_4 - \text{SiR}_2\text{O} \right]_n$	(-2)
$\left[\text{SiR}_2 - \text{C}_5\text{H}_4\text{FeC}_5\text{H}_4 - \text{SiR}_2\text{O} - \text{SiR}_2 - \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 - \text{SiR}_2\text{O} \right]_n$	(7)
Polydimethylsiloxane	-126
Polyphenylmethylsiloxane	-86 (-81)
Polydiphenylsiloxane	~-35

^aObtained by torsional braid analyses or (in parentheses) by differential scanning calorimetry.

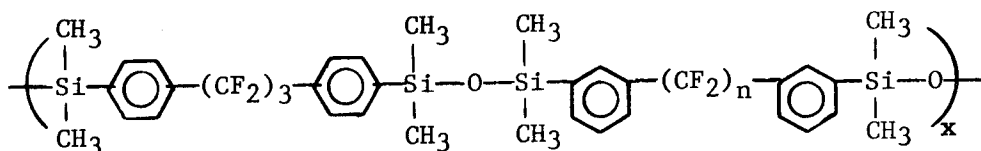
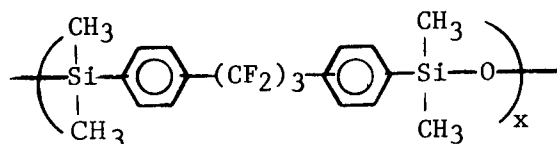


The use of the diphenylcarbonate linkage was further extended to yield a Lexan type material (VIII) having a Tg of 80°C (Tg Lexan = 150°C).



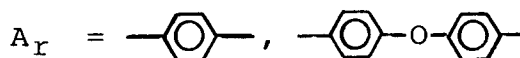
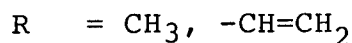
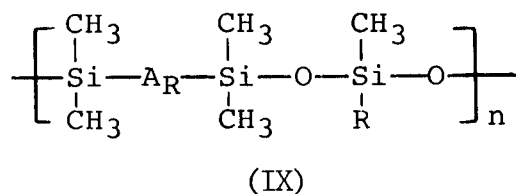
(VIII)

Attempts to improve thermal stability of siloxane modified poly(silarylenes), while at the same time imparting solvent resistance, have also involved the introduction of in-chain perfluoro groups [31]. Polymers of the type



could be crosslinked at room temperature to yield thermoset elastomers having improved thermal and oxidative stability over dimethylsilicones as well as improved resistance to swelling by hydrocarbon solvents.

Lenz has described [19] the effect of vinyl substitution in polymer systems of the type IX.



Resistance to thermal degradation was found to be directly proportional to the extent of vinyl functionality present in the system. It is suggested that the vinylsilane units participate in crosslinking reactions during the early stages of degradation, leading to the formation of more thermally stable residue. In the case of the 4,4'-diphenyl ether analog ($\text{R} = -\text{CH}=\text{CH}_2$ degradation (under N_2) was observed to commence at 490°C with 35% weight loss noted at 740°C . No additional weight loss was observed up to 980°C . However, from studies carried out with crosslinked vinylsiloxane-carboranes (Section 4.3.2c) prolonged aging in air at temperatures of 300°C is expected to lead to oxidative cleavage [32].

3. Silarylene-siloxane block polymers

These materials differ from their random copolymer analogs with regard to improved elasticity, tensile strength and elongation properties. The degree of crystallinity as well as tensile strength exhibited by these polymers is directly proportional to the percent of silarylene functionality incorporated, as can be seen in Tables III and IV [23,28].

In more recent work [32] the mechanical behavior of poly(tetramethyl-p-silphenylene siloxane) (TMPS), and random block copolymers of tetramethyl-p-silphenylene siloxane-dimethyl siloxane (TMPS-DMS) were compared. Results are presented in Table V.

Of additional interest are block copolymers derived from poly(dimethylsiloxane) and perfluoromethylene

TABLE III
EFFECT OF SEQUENCE LENGTH AT CONSTANT MOLE RATIO IN BLOCK COPOLYMERS
OF $(\text{CH}_3)_2\text{SiO}$ (A UNITS) AND $(\text{CH}_3)_2\text{Si-p-C}_6\text{H}_4\text{-Si}(\text{CH}_3)_2\text{O}$ (B UNITS) [23]

Degree of Polymerization of Monomer A	Silphenylene		Minimum Average Arrangement (a/b)	[η] (dl/g)	Tensile Strength(psi)		Elongation (%)
	Mole %	Wt %			Unstressed	Stressed	
18	13	30	18/2.5	1.29	0	0	--
43	13	30	43/6	1.14	553	4525	717
18	13	30	>18/>2.5	0.955	452	3460	667

TABLE IV

EFFECT OF INCREASING p-SILPHENYLENE CONTENT IN BLOCK COPOLYMERS OF
 $[(CH_3)_2SiO]$ (A UNITS) AND $[(CH_3)_2Si-p-C_6H_4-Si(CH_3)_2O]$ (B UNITS) [28]

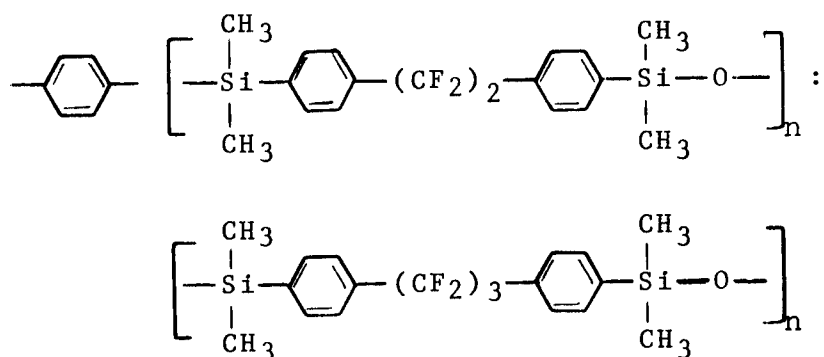
Degree of Polymerization of Monomer A	Silphenylene		Minimum Average Arrangement (a/b)	$[\eta]$ (dl/g)	Tensile Strength(psi)		Elongation (%)
	Mole %	Wt. %			Unstressed	Stressed	
18	13	30	18/2.5	1.29	0	0	--
18	18	40	18/4	1.91	1137	12,100	962
18	25	50	18/6	2.11	1840	15,600	750
18	33	60	18/9	2.00	2085	15,500	643
18	44	70	18/14	1.53	2725	16,000	490

TABLE V
EFFECT OF BLOCK COMPONENT UPON PHYSICAL PROPERTIES [33]
OF POLY(TMPS-DMS) COPOLYMERS

Ratio of TMPS and DMS (wt. %)	Observed T_m ($^{\circ}\text{C}$)	Equilibrium T_m ($^{\circ}\text{C}$)	Melting Temps. ($^{\circ}\text{C}$)	Density (g/cm^3)	Crystallinity Index(density)	Crystallinity Index (DSC)	Storage Young's Modulus Ratio, E'/E'_0
100/0	--	160.0	160.0	1.046	0.59	0.60	420
90/10	139	153.6	156.4	1.036	0.51	0.53	175
80/20	--	145.6	152.1	1.028	0.44	0.50	150
50/50	100	127.3	132.8	1.009	0.28	0.29	20
40/60	69.5	122.2	122.0	0.999	0.18	0.17	6.0
30/70	--	110.5	92.0	0.994	0.13	0.13	2.9

*Dimethylsiloxane

siloxanes of the type

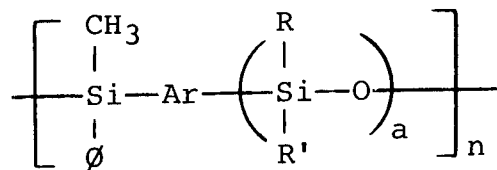


which had improved thermal characteristics over the non-fluorinated analogues [34].

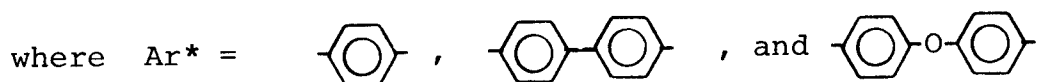
5.2.4 Summary and Recommendations

Based upon the favorable molecular weight [250,000-1,000,000] characteristics of poly(silylarylene-siloxanes) together with the other physical and chemical properties described in the preceding section, this class of materials (including candidates discussed in Section 5.4) shows considerable potential for composite applications. To date, however, the major interest in these polymers has centered on their use as high performance elastomers.

Elastomeric properties are directly proportional to the percentage of siloxane functionality incorporated into the main chain. Although this property is a consideration in the design of processing and handling properties of composite candidates, it has already been shown that as the siloxane content increases, resistance to thermal, oxidative, and chemical degradation decreases. In order to achieve a balance of desired properties, it is suggested that polymers of type (X) be subjected to further investigation.



(X)



R and R' = aryl, alkyl
a = 1-2

Although one would predict that the totally phenylated polymer would be the most thermally stable material, it is anticipated that steric factors would severely limit the molecular weight which could be achieved during synthesis.

For the simplest preferred member of this class (Ar = p-phenylene, R = CH₃, R' = ∅, a = 1) there has been nothing published regarding the synthesis or properties of the disilanol precursor. However, based upon an estimated price of \$3/lb. for methylphenyldichlorosilane it is anticipated that the disilanol will cost \$20/lb. (see Section 5.4.3 for specific details). Assuming a 70% conversion to polymer, a final materials cost of \$30/lb. is projected. The 4,4'-diphenyl ether analogs are not expected to cost considerably more because of favorable pricing of raw materials and the anticipated ease of preparing the disilanol intermediates. Other structural modifications of disilanol are discussed in greater detail in Section 5.4.4.

For polymers where a = 2, the most favorable synthetic pathway appears to be via the silanol-acetoxysilane reaction described in Equation (11). Polycondensation reactions (Equations 4-6) do not favor high yields because of competing reactions while the use of silazanes and bis(ureidosilanes) as intermediates pose difficulties in handling (moisture sensitivity) as well as increased cost. Pricing of polymers derived via the silanol-acetoxysilane reaction are estimated to be slightly higher in cost than alternating poly(silylarylene-siloxanes) where a = 1.

* Those materials in which Ar = ferrocenyl are discussed in Section 5.4

The fact that block copolymers can be prepared does afford some degree of flexibility in the design of the physical properties of candidate materials. Price will be directly proportioned to the percentage of poly(silylarylene-siloxane) incorporated into the block.

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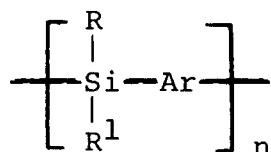
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5.3 Poly(silarylenes)

5.3.1 Introduction

A review [1] dealing primarily with poly(silarylene-siloxanes) addresses, in some detail, this class of materials. The intervening years have generated only limited activity in this area, primarily because of the inability to generate high molecular weight species. This fact has limited the use of low molecular weight poly(silarylenes) to use as additives for various resin and elastomer systems. It has already been noted that the silarylene unit, in addition to acting as a chain termination site during oxidative degradation [2], provides resistance to both acidic and alkaline hydrolysis [3]. It is therefore postulated that these materials, which can be best represented by the general formula I, can, by appropriate



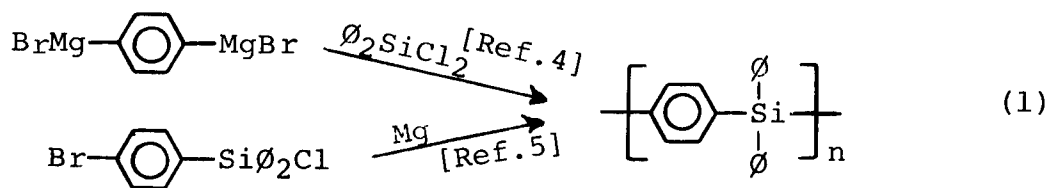
(I)

R and R¹ = alkyl or aryl
Ar = arylene

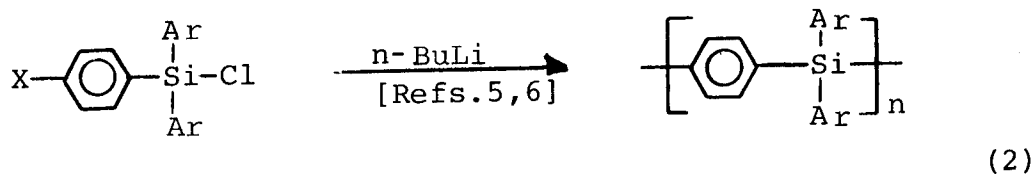
introduction of reactive functionality, be modified to yield potential candidates for advanced composites.

5.3.2 Methods of Preparation

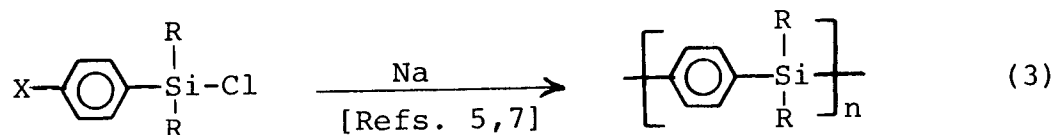
Poly(silarylenes) are most conveniently prepared via organomagnesium (Equation 1) or organolithium (Equation 2) intermediates or by use of sodium coupling techniques (Equations 3 and 4).



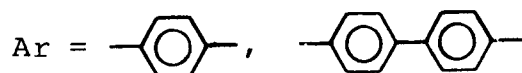
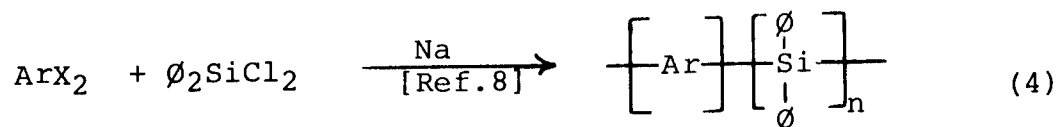
(II)



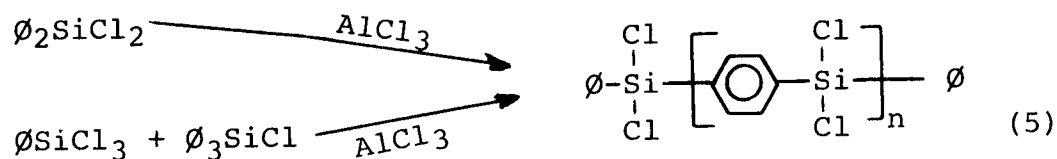
$\text{X} = \text{Cl}, \text{B}$
 $\text{Ar} = \text{aryl}$



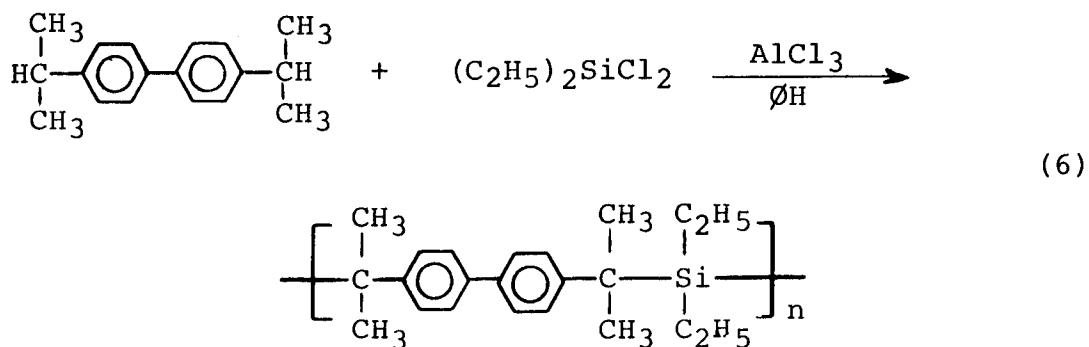
$\text{R} = \phi, \text{CH}_3$
 $\text{X} = \text{Br}, \text{Cl}$



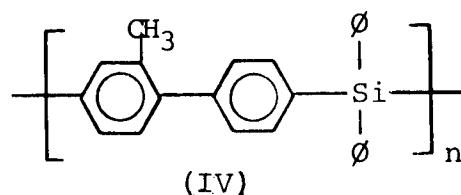
A more direct and less costly synthetic route to this class of polymers involves the use of Lewis acid catalysis as shown in Equations (5) [9] and (6) [10].



(III)



Also of interest is the fact that diphenylsilane can be polymerized in the presence of t-butyl peroxide [11] to yield a material having the following structure (IV):



5.3.3 Physical Properties

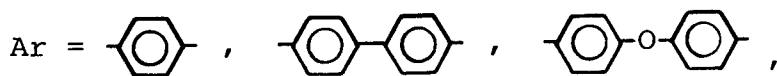
With the exception of thermal stability data, the properties of poly(silarylenes) are not well documented. Thus, the polymer system (II), when prepared via Grignard reaction conditions, was found to be thermally stable at 380°C for short periods and at 300°C for longer periods [4]. When prepared by means of lithiation techniques, the polymer exhibited a melting temperature of 400°C [6] and when generated via sodium coupling conditions the melting point was found to be 420°C with no weight loss experienced during heating at 300°C for 8 hours under nitrogen [5]. The polymer generated under Friedel-Crafts conditions (Equation 6) was not only unusually stable under these conditions but was found to be highly resistant to acids and alkalis [10]. The polymer (IV) derived from the peroxide initiated polymerization of diphenylsilane was found to be highly resistant to high temperatures, losing only 5% of its weight when heated at 900°C for prolonged periods of time [11].

5.3.4 Summary and Recommendations

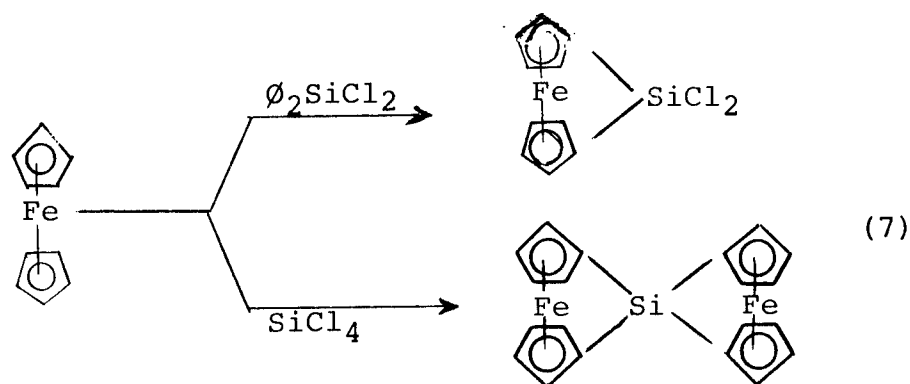
Poly(silarylenes), besides being highly resistant to thermal, oxidative and chemical degradation, afford a unique advantage over the siloxane-type polymers discussed in Sections 5.1, 5.2, and 5.4 in that they are exceptionally stable to hydrolysis. What is lacking, at present, is the ability to generate materials of high enough molecular weight to qualify as candidates for building composites. Based upon the paucity of information in the literature dealing with approaches to this problem, it is difficult to make meaningful recommendations for increasing the molecular weight of these materials short of undertaking a basic development program to achieve this goal.

A secondary concern relative to the selection of this class of materials relates to the costs associated with their synthesis. The economics associated with the use of organometallic intermediates (Li, Mg) are discussed in Sections 5.4.3 and 5.4.4. Since yield data relative to even the low molecular weight polymers in this class is quite sparse, it is difficult to estimate the dollar costs associated with generating candidate materials other than to say that they would be very high (> \$50/lb.). Cost reductions may be possible if the reaction sequences involving either the Friedel-Crafts polymerization of diaryl or dialkyl dichlorosilanes (Equations 5 and 6) or the peroxide initiated polymerization of diarylsilanes leading to materials such as (IV) can be optimized. It should be noted that polymers of type (III) generated via Equation 5 would require subsequent replacement of halogens with aryl, alkyl, or alkoxy substituents.

Provided that a cost effective method of preparing high molecular weight poly(silarylenes) can be developed, there are a number of model systems which could be envisioned as likely composite candidates. Derivatives of (I) in which



and ferrocenyl and R and R¹ are selected from methyl, phenyl, ferrocenyl, and vinyl would be of definite interest. Incorporation of ferrocene as a linking group in the backbone of siloxane polymers has been found to yield materials of high (480°C) thermal stability [3] (see also Sections 4.2 and 5.4). Although poly(silarylene) analogues of these materials have not yet been prepared, recent efforts [12] have demonstrated the feasibility of preparing two key intermediates (IV) and (V) (Equation 7), albeit in very low yield.



The use of silicon-vinyl functionality has been studied in systems of type(I) in which oligomers where Ar is 4,4'-biphenylene, R is alkyl or aryl and R^1 is vinyl were allowed to react with the corresponding silanes ($\text{R}^1 = \text{H}$) [13]. Materials of exceptional thermal stability were obtained. Other silicon-vinyl polymers have been reported [14] and are discussed in Sections 5.2.3 and 5.4.4.

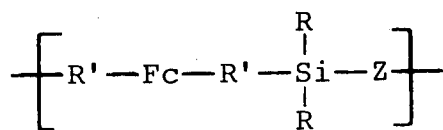
5.3.5 Bibliography

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5.4 Poly(silicon linked ferrocenes)

This class of polymers can be represented by the general formula (I).



(I)



where

R = alkyl, aryl

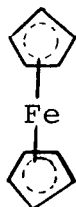
Z = alkylene, arylene,
-O-R'- (but not when
R' = divalent bond)

R' = covalent bond,
alkylene, arylene

R's may be dissimilar

5.4.1 Introduction

Ferrocene's (II) high thermal stability, low toxicity and good hydrocarbon solubility has led to numerous attempts [1, 2, 3] to incorporate the ferrocenyl moiety into a polymer.



(II)

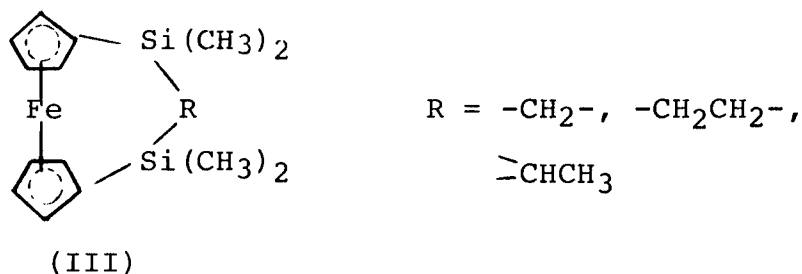
Ferrocene has good stability towards acids and bases [4] and is thermally stable up to 450°C [5, 6]. However, ferrocene decomposes when heated to 350°C in an aqueous suspension in a closed system [5].

Secondary advantages associated with ferrocene materials are high stability to gamma [7] and ultraviolet [8, 9] radiation and high efficiency as a quencher of triplet states [10]. Oxidative stability of ferrocene is poor, but this may

*The abbreviated designation Fc of the divalent heteroannular ferrocenyl radical will be employed in this section.

not be a serious problem because it is converted without molecular weight degradation to the fairly stable ferrocenium ion. Fortunately, structural composites reduce surface exposure of the matrix resin and space environments have very low oxygen concentrations. Both factors lower oxidation rates. Furthermore, oxidation of ferrocene is reversible in many cases and treatment with a variety of mild reducing agents will regenerate the ferrocenium state [5, 11].

A number of ferrocenyl materials, polymeric and non-polymeric, containing silicon directly bonded to the ferrocene nucleus have shown excellent thermal stability [12-15]. Compound (III) ($R = CH_2$) remained unchanged after heating 80 hours at $300^\circ C$ [12] whereas (III) ($R = >CHCH_3$) was produced in 80% yield from (III) ($R = -CH_2CH_2-$) after heating 500 hours at $380^\circ C$ [13].



Low molecular weight organometallic polymers containing various combinations of carborane, ferrocene, and siloxane nuclei showed thermal stability at $454^\circ C$ ($850^\circ F$) [14].

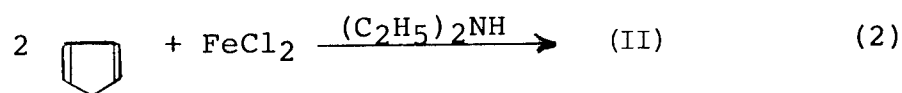
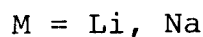
Poly(ferrocenyl) materials not containing silicon have been used to prepare laminates of good quality [16,17]. Therefore the stabler poly(ferrocenyl-siloxanes), of appropriate molecular weight and structure, should represent viable candidates for the preparation of advanced composites.

Low and high molecular weight ferrocene-containing polymers have been prepared in which ferrocene groups are connected by siloxanyl groups. Low molecular weight siloxanyl ferrocene polymers have shown potential as high temperature fluids [18]. High molecular weight poly(ferrocenyl-siloxanes) have shown comparable stability (via TGA) to the corresponding poly(arylenesiloxane) analogs [19,20] (also see Section 5.2). Related poly(ferrocenes) linked with silanyl groups are also discussed in this section but they will receive less attention than the siloxanyl linked materials.

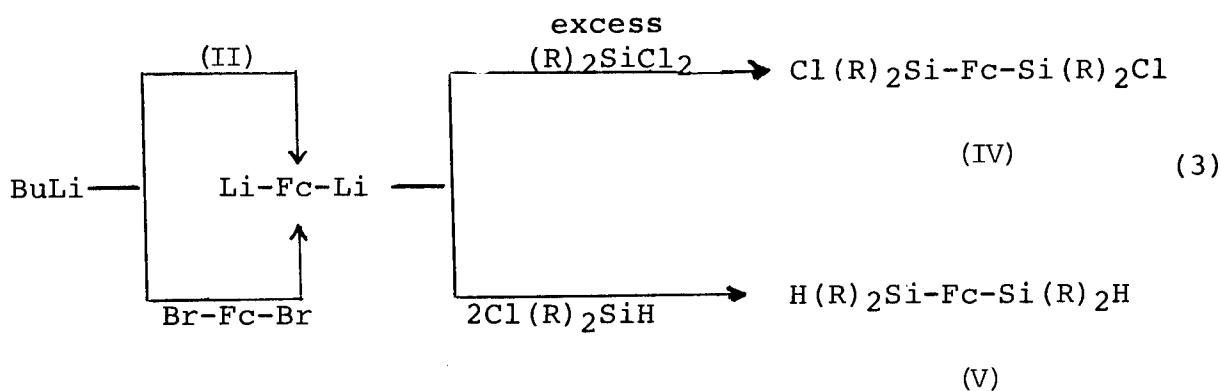
5.4.2 Methods of Preparation

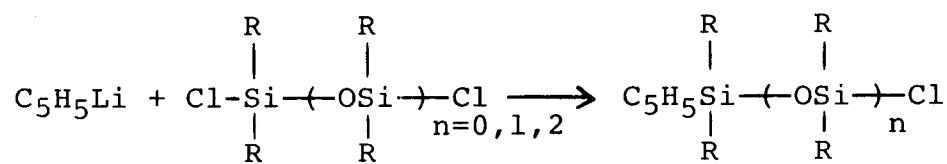
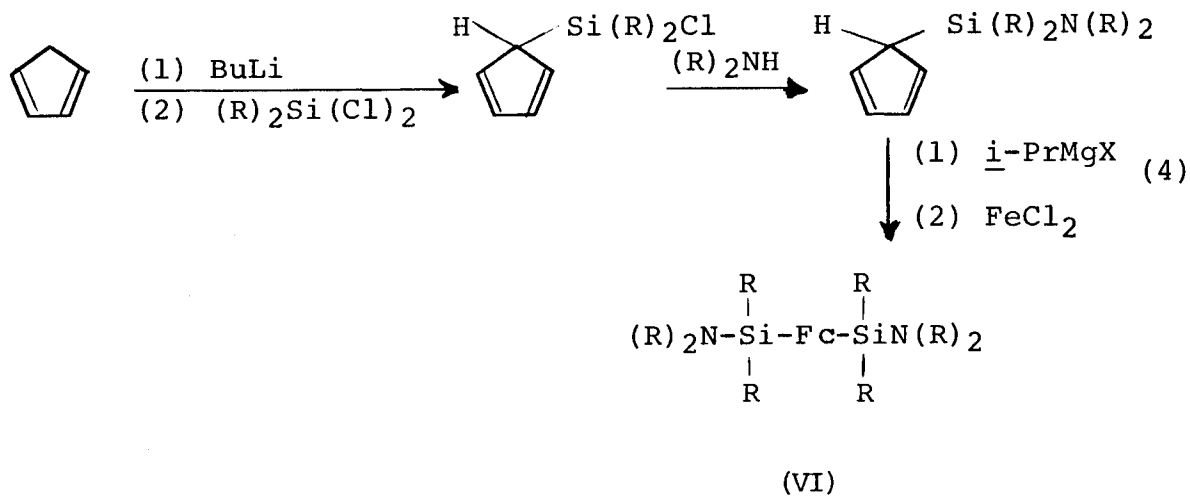
A. Preparation of Intermediates

Ferrocene is usually prepared by the action of FeCl_2 on a metal cyclopentadienide [21,22] or by reaction of cyclopentadiene with FeCl_2 in the presence of a strong organic base such as diethylamine [23a,b] as shown in Equations (1) and (2).

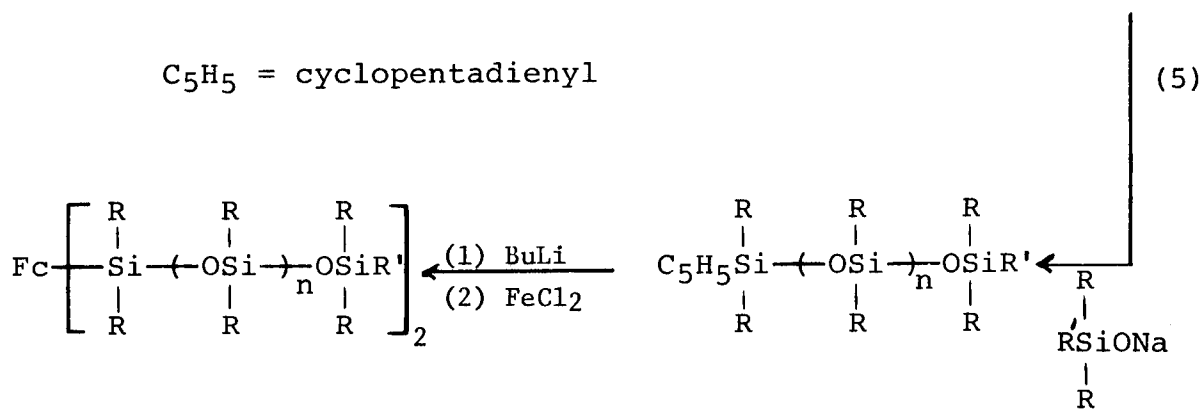


Silylated ferrocene derivatives, that is compounds containing silicon bonded directly to ferrocene, can be prepared by several routes as shown in Equations (3), (4), and (5) [18-20,24,25].





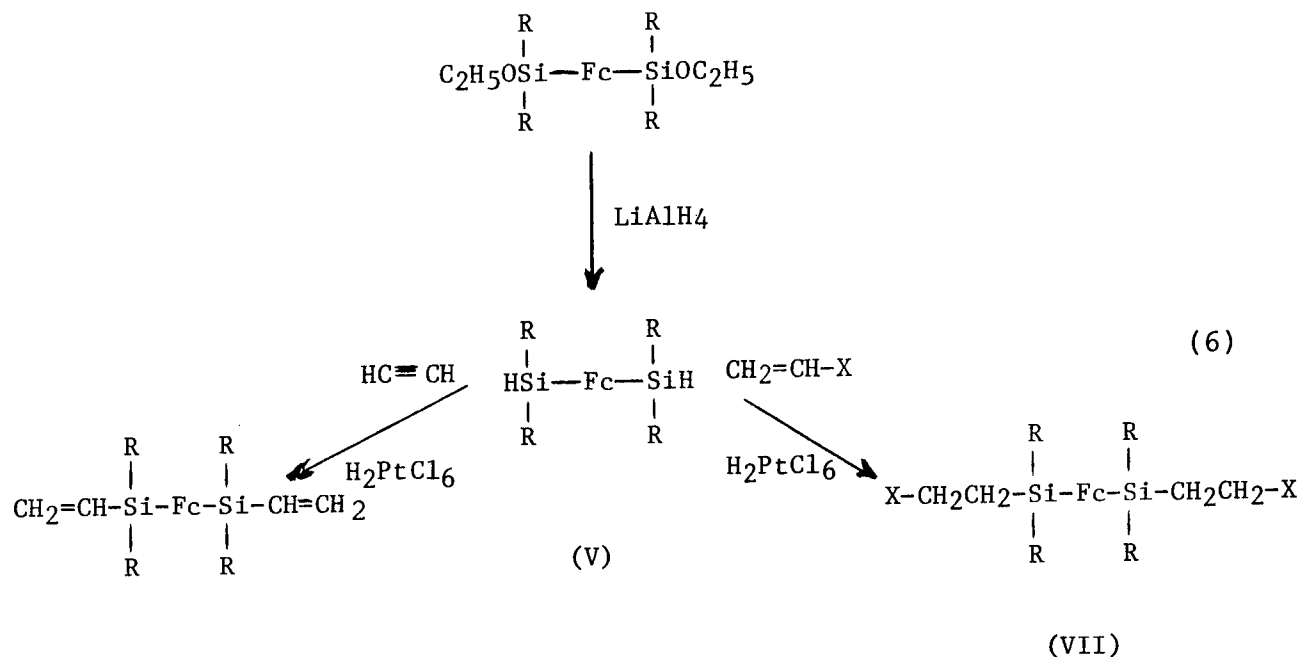
C_5H_5 = cyclopentadienyl



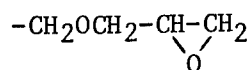
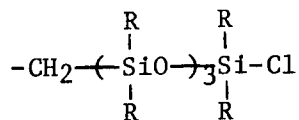
$\text{R} = \text{CH}_3$

Compounds (IV) can be reacted with carboxylic acids or dialkylamines to afford bis(silyl) derivatives such as (VI) which are polymer precursors [19,20].

Other polymer precursors (VII) can be prepared in very high yields ($\geq 80\%$) by hydrosilylation reactions [26,27] of compounds (V) as shown in Equation (6).



where $\text{X} = -\text{CO}_2\text{CH}_3, -\text{CH}_2\text{OSi}(\text{CH}_3)_3,$
 $-\text{CH}_2\text{OH}, -\text{CH}_2\text{NH}_2$

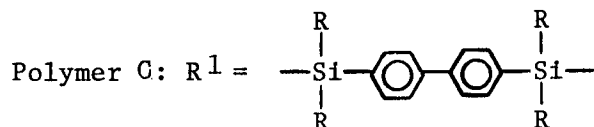
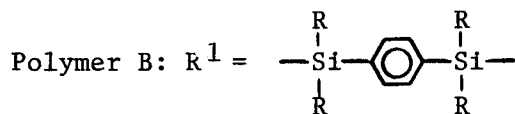
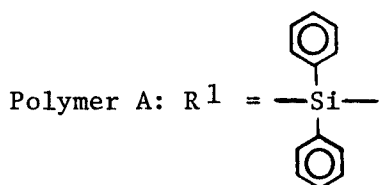
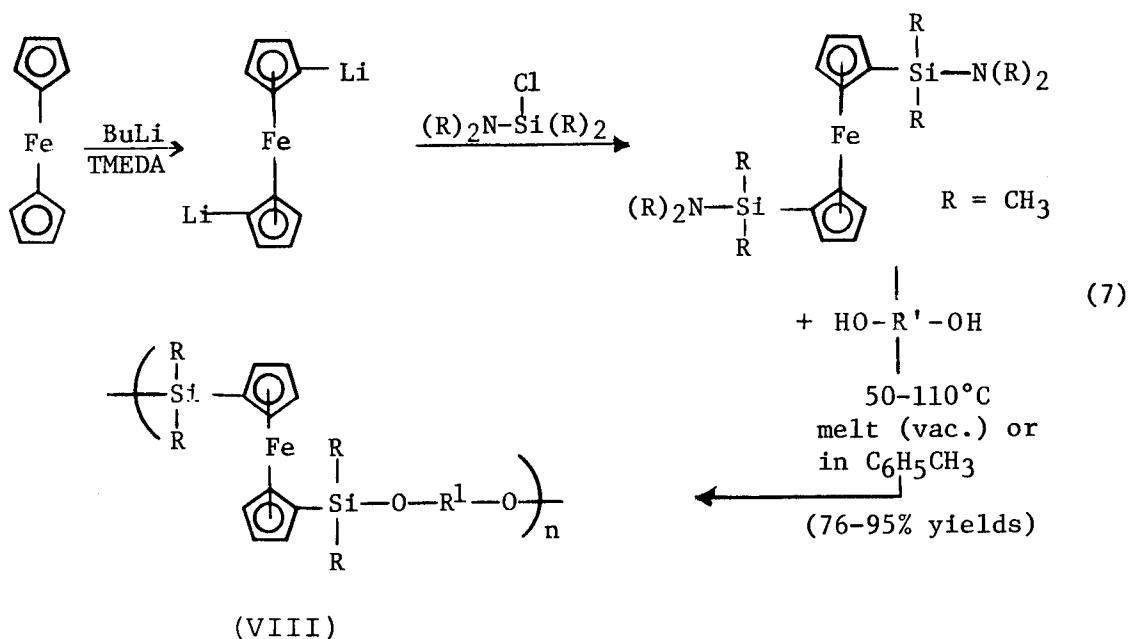


$\text{R} = \text{CH}_3$

B. Preparation of Polymers

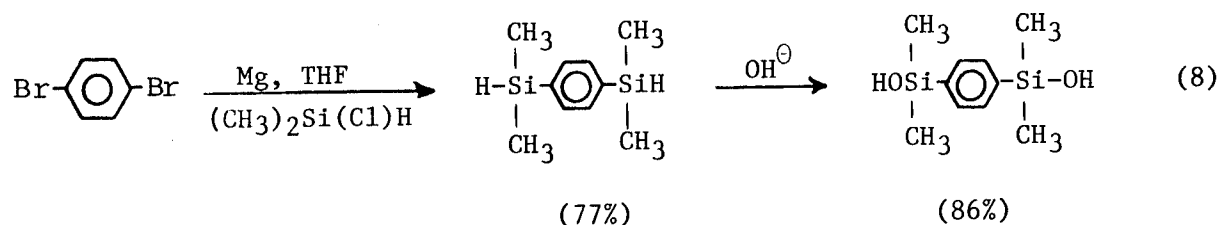
Ferrocenyl siloxane polymers containing -Fc-Si-O links reported prior to 1974 were either largely uncharacterized or low molecular weight materials [25,27-31].

A number of interesting thermally stable poly-(ferrocenyl siloxanes) (VIII) were prepared in good yields by Pittman et al [19,20] using a silyldiol-bis(aminosilanyl)-ferrocene route as shown in Equation (7).

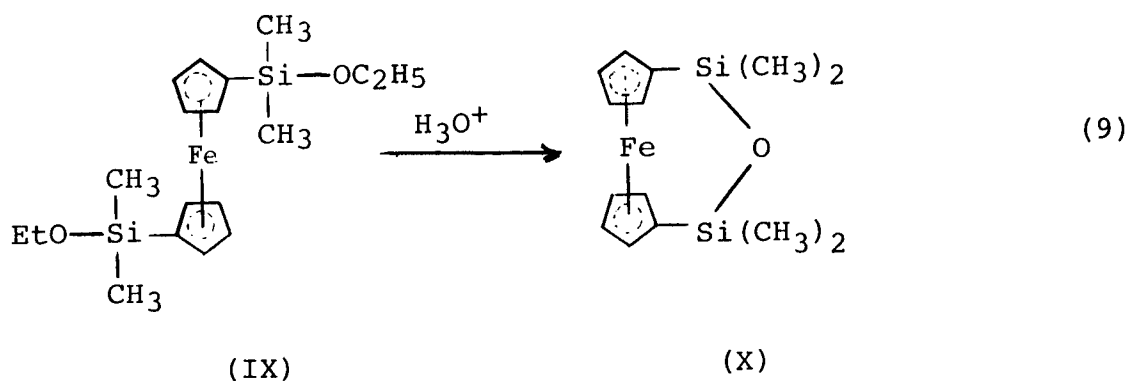


Use of melt polycondensations gave higher molecular weights than solution processes. Polymers shown in Equation (7) ranged in \bar{M}_w from 18,400 to 51,000.

The preparation of silyldiol intermediates is typified in Equation (8) by the preparation of 1,4-bis(hydroxydimethylsilyl)benzene [20].

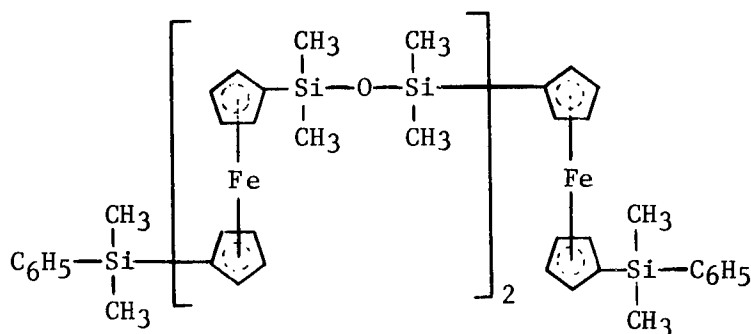


Preparation of poly(ferrocenyl-siloxanes) via intermediate (IX) is unsatisfactory because intramolecular condensation proceeds in high yield [32].



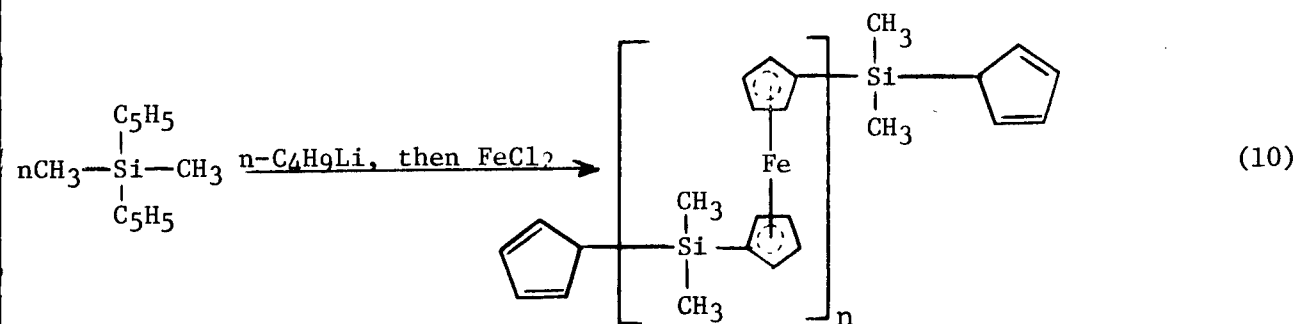
However, the bridged product (X) was converted to linear oligomeric product, such as (XI), by reaction with phenyl lithium followed by reaction with a suitable difunctional chlorosilane, such as 1,1'-bis(dimethylchlorosilyl)ferrocene [24,25]. In this manner a variety of unsymmetrically

substituted siloxanyl ferrocene fluids were prepared which showed very little weight loss (0.1 to 1.1%) after 10 hours at 366°C (N₂) [25].



(XI)

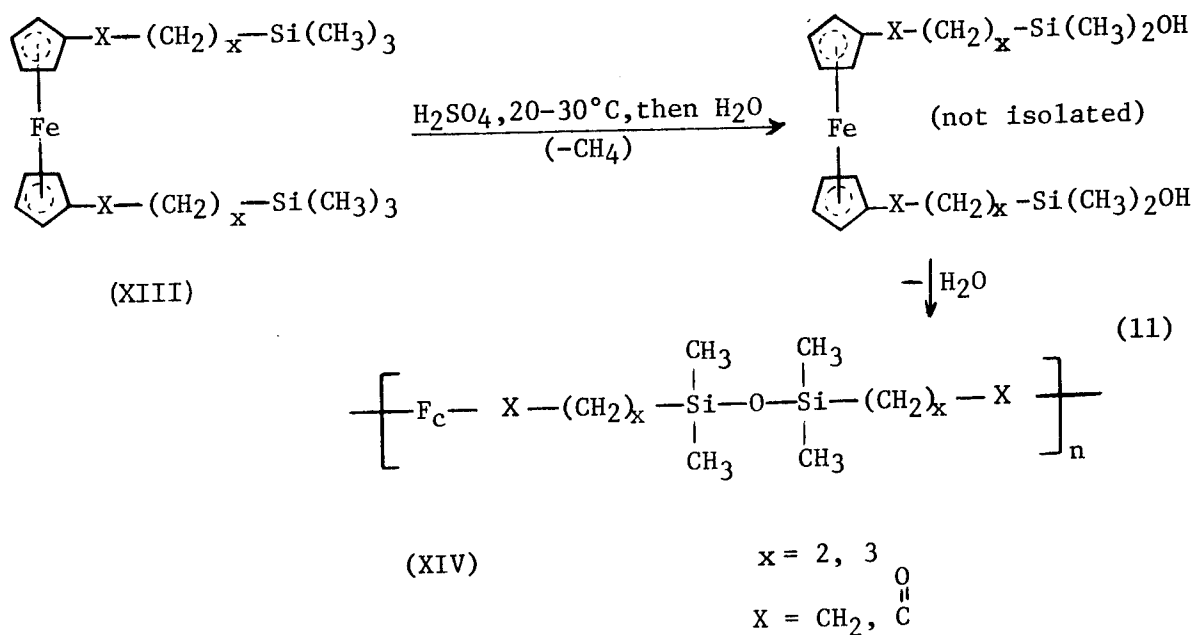
The effect of molecular geometry on reaction course can be seen in the preparation of low molecular weight oligomer products (XII) from dicyclopentadienyl dimethylsilane as shown in Equation (10) [33].



(XII)

Under these conditions compounds such as 1,3-dicyclopentadienyl-1,1,3,3-tetramethylsiloxane and 1,5-dicyclopentadienyl-1,1,3,3,5,5-hexamethyltrisiloxane yield only mononuclear ferrocenophanes.

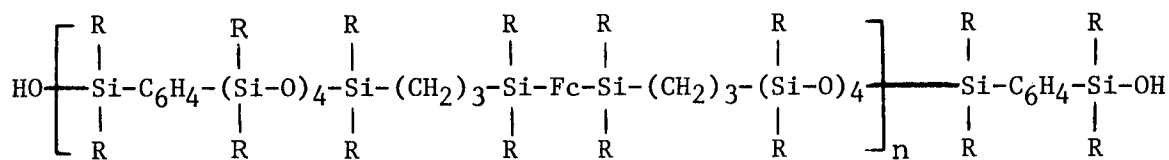
Other poly(ferrocenes) (XIV) linked by siloxanyl groups and carbon atoms were prepared in high yields by Wilkus and co-workers [34-36] as shown in Equation (11).



These workers treated 1,1'-bis(β -trimethylsilylpropionyl)-ferrocene [(XIII) where $X = \text{CO}$ and $n = 2$] with concentrated sulfuric acid at room temperature with subsequent mild dehydration of the hydrolyzed crude product to obtain (XIV) [$X = \text{CO}$, $n = 2$]. The analogous monomers (XIII) where X was CH_2 were obtained by Clemmensen reduction. All polymers were viscous or rubber-elastic resins presumably of low molecular weight. Thermal properties were not reported.

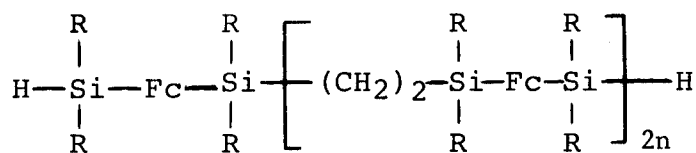
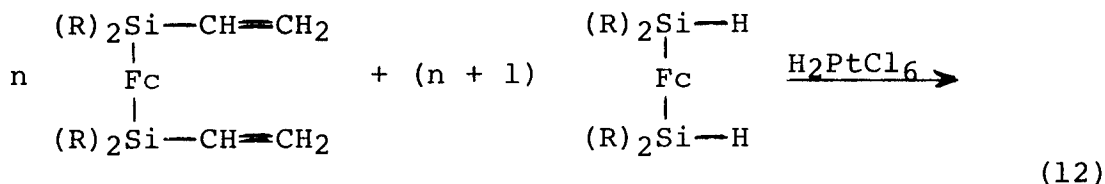
The route to polymers (XIV) shown in Equation (11) was based on earlier work with model silanes $\text{R}-\text{Si}(\text{CH}_3)_3$ which undergo quantitative methyl cleavage [37] yielding silanol and ultimately disiloxane [38].

Polymers with good thermal stability containing both silanyl and siloxanyl bridging groups between ferrocene nuclei have been prepared [27, 31] by partial hydrolysis of 1,1'-bis[3-(7-chloro-1,1,3,3,5,5,7,7-octamethyltetrasiloxanyl)propyldimethylsilyl]ferrocene [obtained from 1,1'-bis(dimethylsilyl)ferrocene and 1-allyl-7-chlorooctamethyltetrasiloxane]. A similar polymer containing *p*-phenylene groups was prepared from the above dichloro compound and 1,4-bis(dimethylhydroxysilyl)benzene. Use of a slight excess of benzene derivative produced polymer (XV) with hydroxysilylphenylene end groups [27].



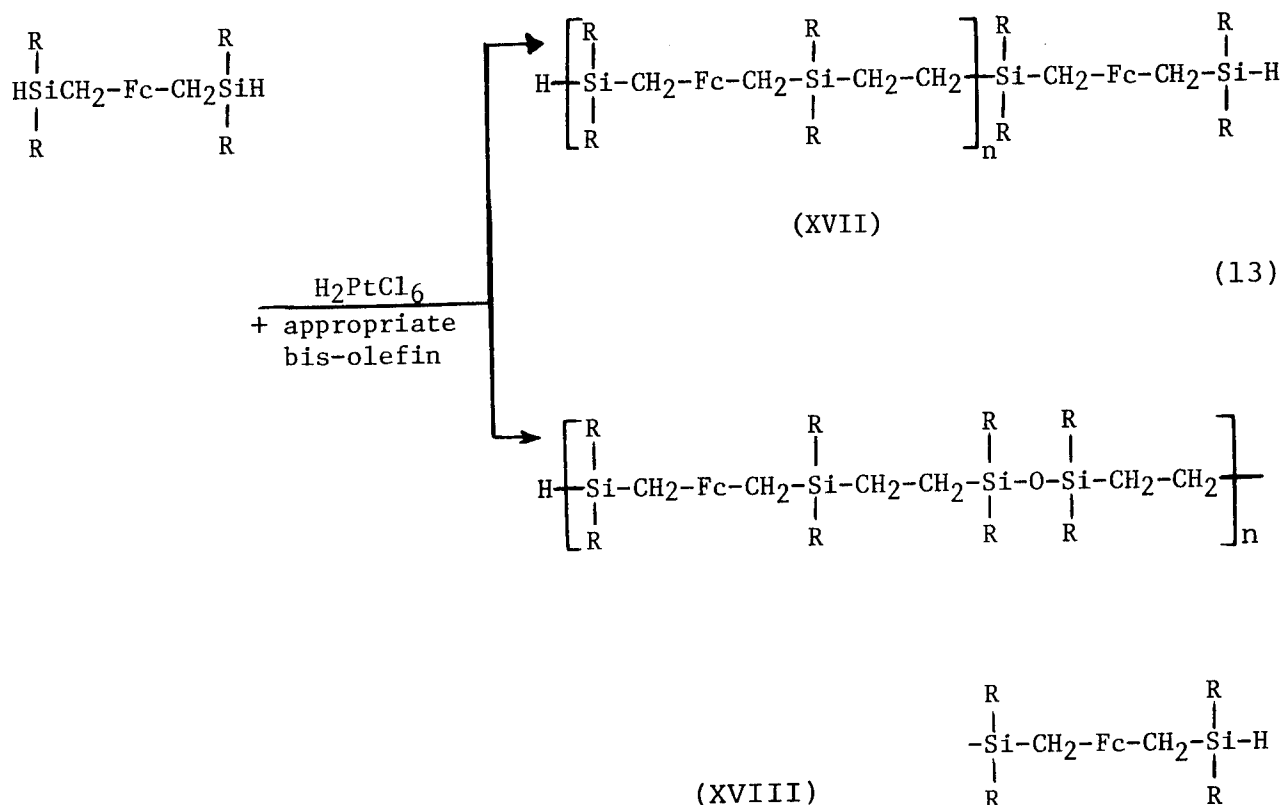
Soluble ferrocenylene(dimethyl)silane polymers, similar to (XII), can also be synthesized [39,40] by reaction of 1,1'-dilithioferrocene and dichlorodimethylsilane. Similarly, use of dilithioferrocene and dichlorodiphenylsilane afford analogous ferrocenylene(diphenyl)silane polymers.

Ferrocenyl silanyl bridged polymers (XVI) with improved thermal stability were prepared via a hydrosilylation reaction exemplified in Equation (12) [26].



(XVI)

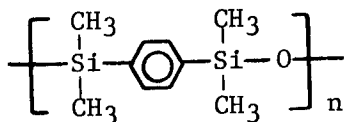
Ferrocene-containing polymers wherein the silicon atoms are not directly bonded to the ferrocene nucleus have also been prepared [31,41] by hydrosilylation reactions, as in Equation (13).



R = CH₃

5.4.3 Properties

Poly(ferrocenyl-siloxanes) (VIII A,B,C) prepared by Pittman [19,20], unlike prior related materials, were of sufficient molecular weight to be cast as tough flexible films and exhibited good fiber-forming properties when drawn from their melts. Individual polymers exhibited (via DSC) values of T_m over a 5°C range and all polymers showed T_m values in the 40-80°C range. Physico-mechanical properties or isothermal aging characteristics were not reported. TGA and DSC data showed that polymer (VIII B) was at least as thermally stable as the related polymer (XIX A) where *p*-phenylene replaced the silyl ferrocenyl moiety.



(XIX A)

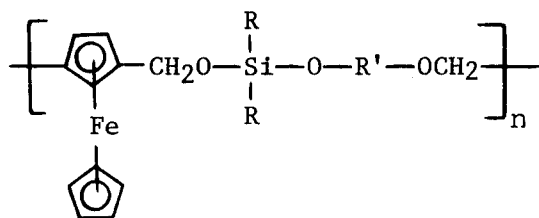
Polymer (VIII B) showed slightly better oxidative stability than polymer (XIX A). In air, the 400°C weight loss (TGA) was 4.5% as opposed to 8.7% for polymer (XIX A). Good hydrolytic stability of these two polymers in refluxing tetrahydrofuran-water (100v/1v) after one hour was observed as shown in Table I.

TABLE I

HYDROLYTIC STABILITY OF POLY(FERROCENYL -SILOXANE) AND
POLY(SILYLARYLENE-SILOXANE) [19]

Polymer	Intrinsic Viscosity (ml/g)		$\bar{M}_w \times 10^{-3}$	
	Initial	Final	Initial	Final
(VIII B)	31.4	28.8	46.8	44.3
(XIX A)	52.2	50.1	105.9	101.4

This stability of the ferrocenyl polysiloxane is in marked contrast to studies obtained with polymer (XX) in which the C-O-Si linkage was associated with hydrolytic instability [42].



(XX)

The data in Table II show that the replacement of -Si(CH₃)₂O- groups by -Si(Ø)₂O groups and the replacement of in chain p-phenylene with ferrocenylene groups increases T_g.

TABLE II

PROPERTIES OF POLYMERS PREPARED BY DIOL-DIAMINOSILANE POLYCONDENSATION [20]

Polymer	Structure (R = CH ₃)	\bar{M}_w	\bar{M}_n	Tg, °C ^a	Tm, °C
(XIX A)	$\text{---}[\text{Si}(\text{R})_2\text{---}\text{C}_6\text{H}_4\text{---Si}(\text{R})_2\text{O}]_n\text{---}$	2.85×10^5	1.11×10^5	-25	--
(XIX B)	$\text{---}[\text{Si}(\text{R})_2\text{---}\text{C}_6\text{H}_4\text{---Si}(\text{R})_2\text{O---Si}(\text{R})_2\text{O}]_n\text{---}$	2.55×10^5	1.09×10^5	-61(-65)	--
(XIX C)	$\text{---}[\text{Si}(\text{R})_2\text{---}\text{C}_6\text{H}_4\text{---Si}(\text{R})_2\text{O---Si}(\text{R})_2\text{O}]_n\text{---}$	2.33×10^5	1.08×10^5	1(-4)	--
(VIII A)	$\text{---}[\text{Si}(\text{R})_2\text{---C}_5\text{H}_4\text{FeC}_5\text{H}_4\text{---Si}(\text{R})_2\text{O---Si}(\text{R})_2\text{O}]_n\text{---}$	1.84×10^4	9.2×10^3	(37)	59
(VIII B)	$\text{---}[\text{Si}(\text{R})_2\text{---C}_5\text{H}_4\text{FeC}_5\text{H}_4\text{---Si}(\text{R})_2\text{---Si}(\text{R})_2\text{O---Si}(\text{R})_2\text{O}]_n\text{---}$	4.68×10^4	1.81×10^4	(-2)	77
(VIII C)	$\text{---}[\text{Si}(\text{R})_2\text{---C}_5\text{H}_4\text{FeC}_5\text{H}_4\text{---Si}(\text{R})_2\text{---Si}(\text{R})_2\text{O---Si}(\text{R})_2\text{O}]_n\text{---}$	5.10×10^4	2.02×10^4	(7)	78

^a Obtained by torsional braid analyses or (in parentheses) by differential scanning calorimetry.

The data in Table III shows that the ferrocenyl polymer (VIII B) has slightly decreased thermal stability compared to polymer (XIX C). However, a more meaningful interpretation would be forthcoming if polymer (VIII A) were compared to polymer (XIX C).

TABLE III

THERMAL PARAMETERS OF SELECTED OXYSILANE POLYMERS [20]

Polymer	Temperature at which 10% weight loss occurred at 4°/min. under N ₂ , °C	Temperature at which exotherm was observed in DSC under N ₂ , °C
(XIX A)	475	--
(XIX B)	380	445
(XIX C)	445	490
(VIII B)	440	--

The poly[(silanyl-siloxanyl)ferrocene] (XV) discussed earlier showed relatively good thermo-oxidative stability (CO₂ atmosphere). Accumulated percent weight losses are shown in Table IV.

TABLE IV

THERMO-OXIDATIVE STABILITY OF POLY[(SILANYL-SILOXANYL)FERROCENE] (XV)

After 2 hrs., 200°C	After 2 hrs., 250°C	After 2 hrs., 300°C
0.6	2.3	7.7

Increasing molecular weight and/or T_g would most likely result in better thermal stability.

The ferrocenyl silanyl bridged polymers (XVI) showed improved thermal stability relative to polymers (XV). A weight loss of 0.3% was observed after 6 hours at 300°C, whereas the accumulated weight loss after 2 hours additional heating at 350°C was 17.1% [26].

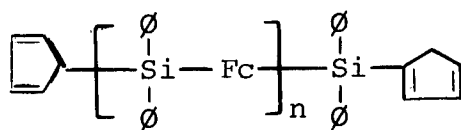
Silanyl containing poly(ferrocenes) and silanyl-siloxanyl containing poly(ferrocenes) wherein the silicon is not directly bonded to ferrocene showed even better thermo-oxidative stability as shown in Table V.

TABLE V
THERMO-OXIDATIVE STABILITY OF SOME POLY(SILANYL)-
AND POLY(SILOXANYL)-FERROCENES [26, 41]

Compound	Softening Point (°C)	Accumulated Weight Loss (%)	
		After 6 hr @ 300°C	After Additional 2 hr @ 350°C
(XVI)	92-94	0.3	17.1
(XVII)	90-96	5.1	13.0
(XVIII)	Oily at room temp.	4.3	11.2

These data suggest that at the higher temperature of 350°C, the ferrocene-silicon bond is more susceptible to fission than is the ferrocene-methylene bond. The reported [12] ready isomerization of 1,1'-disilyl ferrocenes to homoannularly substituted ferrocenes at 300°C supports this view. However, further studies are necessary to elucidate the degradation mechanisms.

Soluble ferrocenylene (diphenyl)silane polymers [39,40] (XXI) of molecular weight 1400 to 1700 are high melting (>350°C),



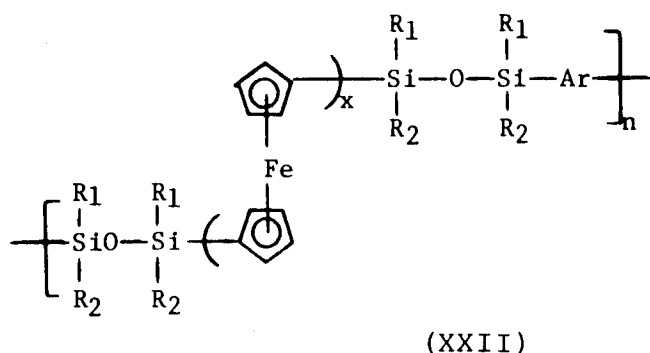
(XXI)

but despite this, TGA (in nitrogen) showed incipient weight loss at 200° to 250°C. These results suggested a useful service life of dimethylsilane- and diphenylsilane-bridged polymers to be 250°C or less.

The difunctional dimethylsilyl ferrocenes (VII) were employed to prepare linear soluble condensation polymers such as polyesters, polyamides, and polyurethanes [27, 31]. These polymers had softening points of 70° to 130°C and showed poorer stability than the poly(ferrocenyl-siloxane) (XV) and therefore will not be discussed further.

5.4.4 Summary and Recommendations

Poly(ferrocenyl-siloxanes) of structure (XXII) show potential as matrix resins for advanced composites.



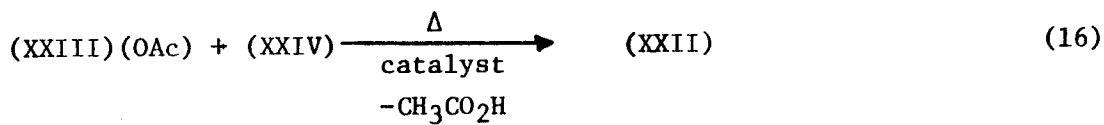
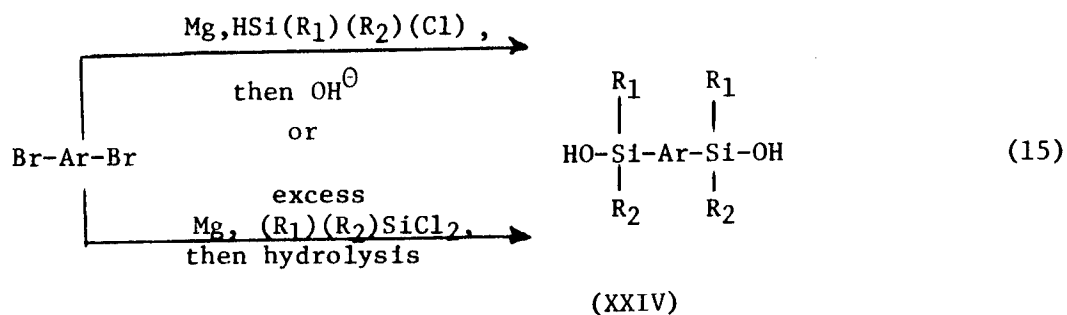
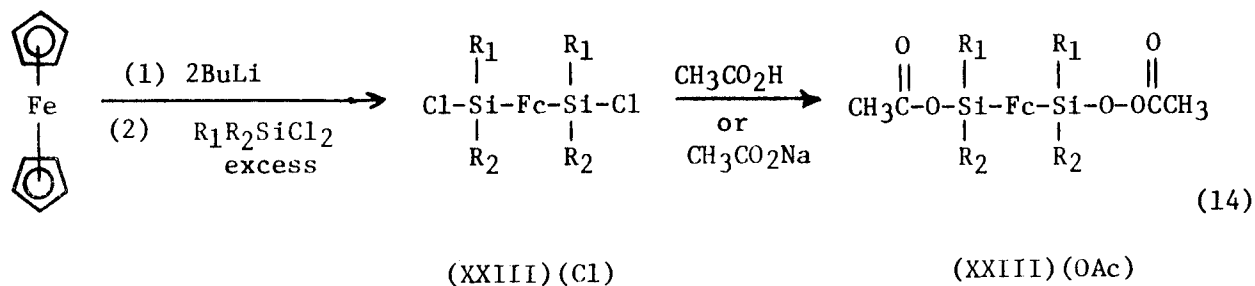
where $R_1 = \text{CH}_3, \text{C}_6\text{H}_5$
 $R_2 = \text{C}_6\text{H}_5$
 $\text{Ar} = \text{arylene, preferably}$
 $\text{Z} = \text{covalent bond, } -\text{O}-,$
 $\text{--S--}, \text{--}\overset{\text{O}}{\parallel}\text{C--}$
 $x = 1-3$
 $R's \text{ may be dissimilar}$

To realize this potential it will be necessary to increase molecular weight as well as to significantly raise physical transition temperatures over prior art materials. In addition, provision should be made for conversion to thermosetting materials which will be load-bearing at $\geq 300^\circ\text{C}$ and eliminate susceptibility to thermo-oxidation.

Poly(ferrocenes) linked via silanyl or alkylene groups are not recommended for further study because these materials were produced in very low molecular weights and/or show considerably poorer thermal stability than poly(siloxane linked ferrocenes) (VIII). Poly(silicon linked ferrocenes) such as types (XV)-(XVIII) prepared by hydrosilylation reactions contain $-\text{CH}_2\text{CH}_2-$ sites which would greatly reduce thermo-oxidative stability and lower T_g and T_m . The same undesirable effect is

anticipated by the presence of $-\text{CH}_2$ sites adjacent to ferrocene nuclei.

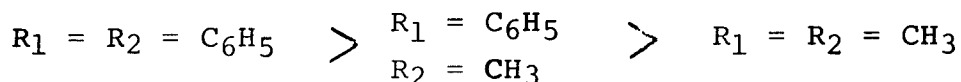
The preferred method of synthesis of (XXII) ($x = 1$) is outlined in Equations (14)-(16).



The alternate preparation of intermediate (XXIII) (Cl) via silylation of cyclopentadiene with subsequent metallation and reaction with FeCl_2 affords lower yields than the route shown in Equation (14) [19].

Preparation of arylene dibromide intermediates (Eq. 15) proceeds in good yield with para or para-para' orientation strongly predominating. Silylation of unisolated dibromide can be accomplished in situ, after removal of HBr . Favorable reactivity and geometry make biphenyl (36¢/lb*) and diphenyl ether (85¢/lb*) very attractive substrates for the preparation of arylene disilanol. Meta orientation is not anticipated because bromination studies of model mono-halobenzenes afford 87-89% para orientation and 11-13% ortho orientation [43]. Recrystallization should readily remove ortho-arylene disilanol from the desired higher melting para-oriented isomers.

The order of thermo-oxidative stability as well as the order of increasing T_g and T_m for polymer structure (XXII) is as follows:



Preparation of the completely phenylated polymer is not recommended because the polycondensation reaction would be sluggish and possibly prone to undesirable side reactions, therefore limiting achievement of very high molecular weights. The case where $R_1 = \text{CH}_3$ and $R_2 = \text{C}_6\text{H}_5$ should represent the best compromise of polymer properties with attainment of high molecular weights.

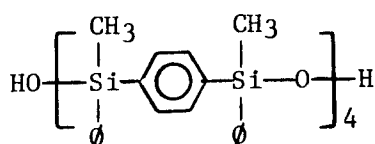
Preparation of polymers via the silanol-acetoxy-silane condensation method [44] is preferred over the bis(ureido)-silanediol method [45-47a,b] (also see Sections 4.3.2c and 5.2.2). The ureido intermediates are extremely moisture sensitive and potentially much more expensive than the analogous bis(acetoxy-silanes) (XXIII) (OAc).

Molecular weights of at least 250,000, preferably 1 million, should be sought to achieve the full potential of properties. The current state-of-the-art has produced poly-(siloxanyl linked ferrocenes) (VIII A,B,C) with molecular weights to 51,000 [20]. However, poly(arylenesiloxanylenes) have been prepared by a silanol-acetoxysilane condensation in

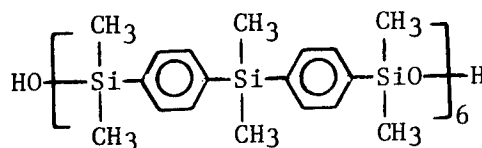
*Asterisked prices are from Chemical Marketing Reporter, February 5, 1979. All other prices are considered very approximate. Volume prices will arbitrarily be defined as being based on an annual usage of 100,000 lbs.

molecular weights of 250,000 to 300,000 [44] and in one instance to 600,000 [48]. The importance of molecular weight on properties proved to be quite dramatic for poly(carborane-siloxanes) [46] (also see Section 4.3.2c).

The simplest and least expensive polymers comprise the case where x is unity and Ar is chosen from a simple divalent arylene substituent. If these polymers do not afford sufficiently high physical transition temperatures then two other structural variations should be considered; (a) use of oligomeric poly(ferrocenyl) groups, i.e., $x = 2$ or 3, and (b) use of poly(silarylene)diols such as (XXV) and (XXVI).



(XXV)



(XXVI)

Oligomeric poly(ferrocenes) can be easily prepared by reaction of dilithioferrocene and 1,1'-dibromoferrocene in the presence of CoCl_2 [1,49]. Diols (XXV) and (XXVI) show very good solubility in many organic solvents and have been prepared [50] in 78-83% yields from $p\text{-C}_6\text{H}_4[\text{Si}(\text{CH}_3)(\text{Cl})]_2$ and $[p\text{-(Cl)(CH}_3)_2\text{-SiC}_6\text{H}_4]_2\text{Si}(\text{CH}_3)_2$, respectively. Low molecular weight poly(ferrocenes) have shown very good thermal stability (TGA, argon), giving relative residual weights of about 85 and 75% at 600°C and 800°C, respectively [51].

Introduction of methylvinylsilylene cure sites to increase thermal stability of poly(silarylene-siloxane) elastomers [47a,b] is discussed in Section 5.2.3. Unfortunately, this cure site has been found to be the weakest link thermally in poly(carborane-siloxane) vulcanizates when heat aged in air at 315°C [46]. If this instability extrapolates to poly(siloxanyl-ferrocenes), then other means of removing thermoplasticity may have to be employed.

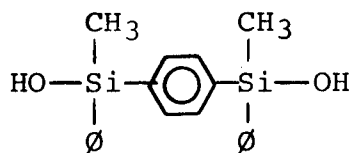
High performance advanced composites require retention of properties at temperatures in excess of 300°C, often in the presence of oxygen. Antioxidants or reducing agents will probably be necessary to insure desired performance.

Mild reducing agents such as zinc dust and antioxidants such as arsenic thioarsenate (AsAsS_4) and ferric oxide may be employed. The thioarsenate was found to be very beneficial in improving thermal characteristics of a poly(benzimidazole) adhesive [52]. Tensile shear strength after 10 hours at 370°C was found to be five times (2000 vs. 401 psi) that of the control without thioarsenate. Ferric oxide, particularly when derived by thermal decomposition of iron pentacarbonyl, was found very effective in retaining elastomeric properties of poly(carborane-siloxane) vulcanizates aged 1,000 hours in air at 315°C [53].

Ferrocene can be prepared readily in high yield and high purity from cyclopentadiene, base (e.g., CH_3ONa), and FeCl_2 [21,22]. Cyclopentadiene is readily produced in high conversion by thermal cracking of dicyclopentadiene, currently available at 11¢/lb.* Ferrous chloride can be prepared in situ from powdered iron and FeCl_3 (19¢/lb*). The potential price of ferrocene is estimated at $\leq \$1/\text{lb}$.

The preparation of bis(silyl)derivative (XXIII) (C1) utilizes butyl lithium (about \$3-\$4/lb), ferrocene ($\leq \$1/\text{lb}$), and most likely methylphenyldichlorosilane (estimated at a potential cost of \$3/lb). It is anticipated that (XXIII) can be prepared in yields of $\geq 75\%$. Therefore its approximate cost, in volume, is estimated at \$10/lb. This assumes good recovery of excess dichlorosilane intermediate.

The simplest desirable arylenedisilanol is (XXVII)



(XXVII)

*

Asterisked prices are from Chemical Marketing Reporter, February 5, 1979. All other prices are considered very approximate. Volume prices will arbitrarily be defined as being based on an annual usage of 100,000 lbs.

which would be prepared by aqueous alkali treatment of the product derived from the reaction of magnesium (99¢/lb*), 1,4-dibromobenzene, and methylphenyl chlorosilane. 1,4-Dibromobenzene can be prepared in good yield from benzene and bromine (55¢/lb*) and could be priced at about \$2.51/lb. Assuming a potential price of \$5/lb for methylphenyl chlorosilane and conversion of 1,4-dibromobenzene to (XXVII) in 65% yield [note: Pittman [20] similarly prepared 1,4-bis(hydroxydimethylsilyl)benzene from 1,4-dibromobenzene in overall yield of $0.77 \times 0.86 \times 100\% = 66\%$], the potential price of disilanol (XXVII) would be about \$23/lb. The price of disilanol could be reduced to about \$20 by replacing methylphenylchlorosilane with methylphenyldichlorosilane (\$3/lb).

Polymer (XXII), $R_1 = CH_3$, $R_2 = C_6H_5$, $x = 1$, is anticipated to be prepared in $\geq 75\%$ yield. Using the above prices of monomers the polymer cost is estimated to be \$36/lb. Any further sophistication of polymer structure, such as increasing x , having $R_1 = R_2 = C_6H_5$, use of silanediols (XXV) or (XXVI), or use of uncommon cure sites would increase the cost of polymer.

There is some likelihood that aromatics can be silylated at elevated temperatures using appropriate silane halide(s) and aromatic hydrocarbon in the presence of catalyst(s). If such a process were to be demonstrated commercially, the price of chlorosilanes of structure $(R_1)(R_2)-SiH(Cl)$ would be considerably reduced. The price of polymer would decrease accordingly.

5.4.5 Bibliography

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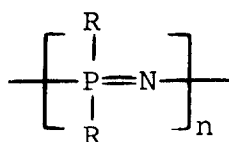
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5.5 Poly(organophosphazenes)

Poly(organophosphazenes), also called poly(phosphonitrilics), are linear polymers defined by the general structure (I):



where R = Alkyl (R'), aryl (Ar),
OR', OAr, NHR', NHAr

(I)

Cyclic oligomers will only be discussed relative to the preparation of linear high molecular weight polymers. Linear or 3-dimensional polymers containing cyclic phosphazene structures or polymers containing significant amounts of nonphosphazene structures will not be reviewed critically because too little is known about these materials or they have not shown sufficient promise to date (also see Section 4.1.2f).

5.5.1 Introduction

Phosphazenes, which are isoelectronic with siloxanes, have been receiving increasing attention in recent years. Several excellent reviews [1-6] have appeared on poly(organophosphazenes). Current interest in these materials centers on their ability to be formulated into highly fire-retardant low smoke producing compositions [7-13] and their potential use in biomedical applications [3].

The most common method of synthesis, discussed in Section 5.5.2, allows for unprecedented structure-property control. High molecular weight elastomers with T_g values of -70°C as well as high melting plastics can be prepared by judicious choice of R groups in (I). Many poly(organophosphazenes) are film-forming thermoplastics and several are fiber formers.

Other properties besides fire-retardancy and extremely simple physical property control that make poly(organophosphazenes) attractive are:

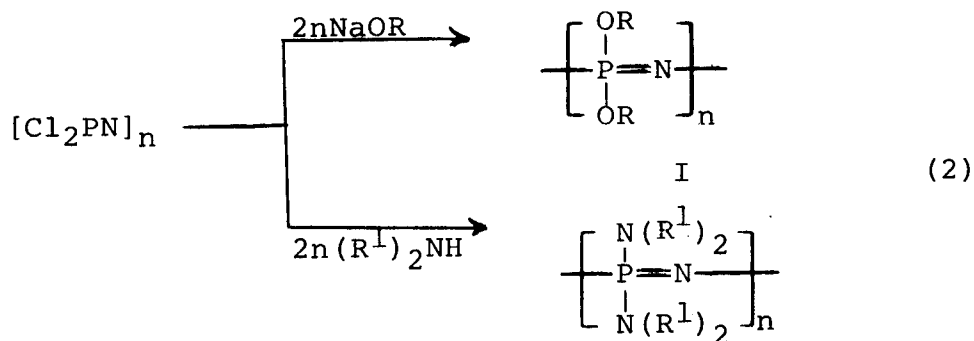
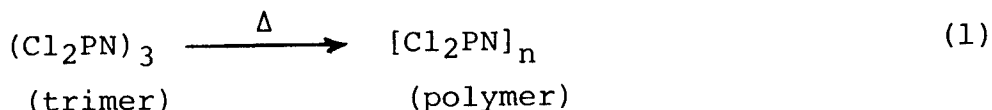
Wide temperature serviceability,
Hydrolytic stability,
Ease of processing and curing,
Excellent electrical properties,
Radiation resistance, and
Environmental safety.

To date, the one limiting property of poly(organophosphazenes) is that of thermal stability. Little work has been reported on the use of poly(organophosphazenes) for the preparation of composites. No outstanding performance was observed in several instances.

A highly fluorinated poly(phosphazene) [PNF[®]] and a poly(aryloxyphosphazene), both containing a small amount of cure site, are currently available from The Firestone Tire & Rubber Company (Akron, Ohio).

5.5.2 Methods of Preparation

The most widely used method of synthesis for the preparation of linear poly(organophosphazenes) is shown in Equations (1) and (2).

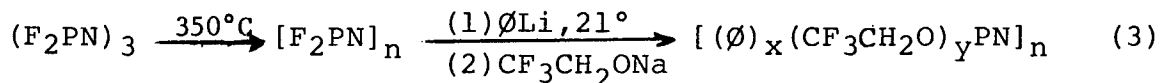


where R may be selected from alkyl, aryl, R¹ may be selected from H, alkyl, aryl with the proviso that both R¹'s are not H, ethyl (or higher alkyl), and/or aryl. Both R's or R¹'s may be dissimilar.

Very high or low molecular weight poly(dichlorophosphazene), $[\text{Cl}_2\text{PN}]_n$, can be prepared by a ring opening polymerization of hexachlorocyclotriphosphazene, $(\text{Cl}_2\text{PN})_3$, depending on polymerization conditions and presence of catalyst. The $[\text{Cl}_2\text{PN}]_n$ polymer is extremely hydrolytically unstable and readily crosslinks in the presence of water. Conventionally, bulk polymerizations are carried out in sealed evacuated tubes at 250° to 270°C for periods of 6 to 48 hours. Alternately, high molecular weight polymer can be prepared easily by a catalytic solution polymerization [14]. This latter mode of preparation is advantageous because it employs ordinary laboratory glassware at atmospheric pressure at temperatures of about 200°C.

The conversion of $[\text{Cl}_2\text{PN}]_n$ polymer to $[(\text{RO})_2\text{PN}]_n$ polymer is generally performed at 25°C to 130°C, depending on the nature of RNa, in ethereal and/or aromatic hydrocarbon solvents. In this manner quantitative replacement of P-Cl sites is achieved and molecular weights in excess of one million [15] are possible. Use of more than one alkoxide affords random copolymers and higher interpolymers. It is therefore not only possible to tailor physical properties of the final polymer, but one can control the amounts of selected cure sites that can be incorporated into it. These cure sites allow for crosslinking by conventional methods (organic peroxides, sulfur accelerated, radiation).

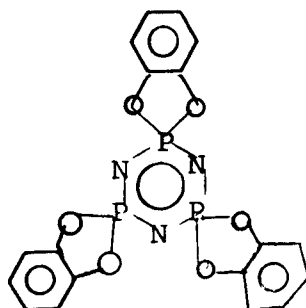
A variation of the chemistry in Equations (1) and (2) is shown in Equation (3). This is a highly significant modification because poly(organophosphazenes) with high phosphorus-carbon content can be prepared [16,17] from soluble high molecular weight precursor. At a phenyl/ $\text{CF}_3\text{CH}_2\text{O}$ ratio of 62/38, a film-forming polymer with T_g of 60°C and molecular weight of 1.2×10^6 was obtained [16].



Unfortunately, there are several drawbacks to this approach. First, the polymerization requires very high temperatures in a high pressure autoclave. Second, expensive perfluorinated solvents are used to dissolve the poly(difluorophosphazene). Third, high ($\geq 80\%$) substitution of P-Cl sites by the organo-metallic reagent leads to extensive molecular weight degradation.

This necessitates reaction of residual P-Cl with another nucleophile (e.g. $\text{CF}_3\text{CH}_2\text{ONa}$).

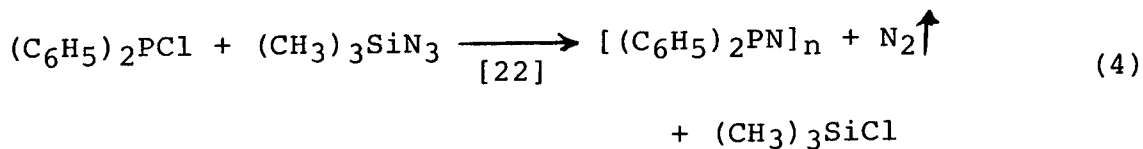
Attempts to prepare linear poly(organophosphazenes) from organo substituted cyclotri(or tetra)phosphazenes, $[(\text{R}_2\text{PN})_3, 4]$, have generally been unsuccessful. However, there are some reports claiming successful ring opening polymerization. The cyclic oligomers $[(\emptyset)_2\text{PN}]_x$ and $[(\emptyset\text{O})_2\text{PN}]_x$ are reported to polymerize at $250^\circ\text{--}300^\circ\text{C}$ using an acid catalyst [18]. Tris(o-phenylenedioxy)phosphonitrile trimer (II) was reported to undergo thermal polymerization [19].

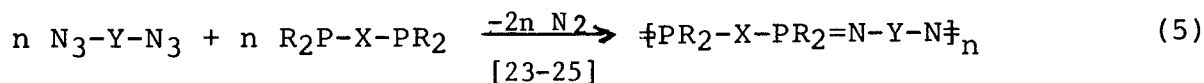


(II)

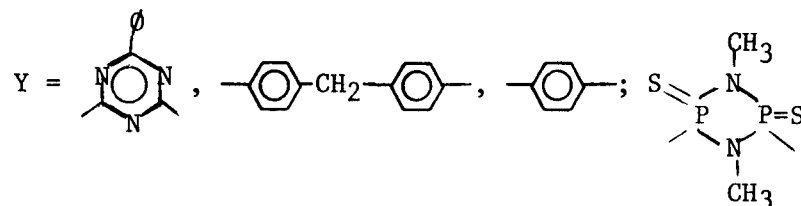
Several cyclotriphosphazenes containing both organic ligands (e.g. \emptyset , $\text{CF}_3\text{CH}_2\text{O}$) and P-Cl sites have been homopolymerized and copolymerized with $(\text{Cl}_2\text{PN})_3$ [20,21].

Other less attractive methods of preparing poly(organophosphazenes) involve reactions of phosphines with azides, amines, or ammonium halides as shown in Equations (4)-(7).

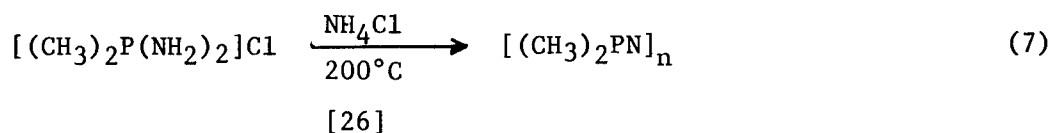
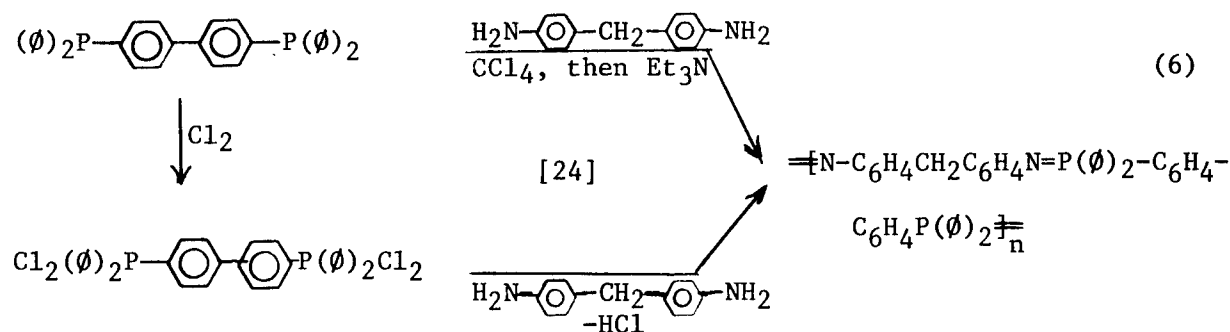




where $X = \text{-(CH}_2\text{)}_4\text{, -C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-, -C}_6\text{H}_4\text{-; -CH}_2\text{)}_n$



$R = \text{-C}_6\text{H}_5$



The azide reaction (Equations 4 and 5) is hazardous because of the potential for explosion. The polymers produced in Equations (5) and (6) suffer in that the degree of polymerization varied from 3 to 12 despite many adjustments in reaction conditions [24].

A survey of the above methods of preparing poly(organophosphazenes) leads to the inescapable conclusion that the ring opening polymerization with subsequent derivatization is the method of choice to prepare high molecular weight polymers with diverse structures.

5.5.3 Properties

(a) Physical Transitions

Physical transitions (T_g , T_m) of poly(organophosphazenes) vary widely and are highly dependent on two factors; the type of substituent bonded to phosphorus and the number of different kinds of substituents bonded to phosphorus. Table I summarizes transition and decomposition temperatures representative of poly(organophosphazenes). Poly(arylamino-phosphazenes) have significantly higher T_g values than their aryloxy analogs, but their T_{dec} values are at least 100°C lower.

Based on TGA, $[(C_6H_5O)_2PN]_n$ and its halogenated derivatives appear to offer the best combination of properties as candidates for advanced composites. T_m and T_d are not given for poly(alkoxyphosphazenes) because these materials, in addition to being elastomers with very low T_g values, should isomerize to hydrolytically unstable poly(phosphazanes) at temperatures of 130°C and above. This has been conclusively demonstrated for alkoxycyclotriphosphazenes [30,31].

(b) Hydrolytic Stability

Relatively little is reported on the hydrolytic stability of thermoplastic poly(organophosphazenes). $[(CF_3)_2PN]_n$ polymer is insoluble in all common organic solvents and shows no change upon refluxing with H_2SO_4 , HNO_3 , or $HClO_4$ [32,33]. However, this polymer undergoes partial hydrolysis with 10% NaOH. Impure poly(diphenylphosphazene) shows excellent stability to refluxing 0.1 M HNO_3 and 0.1 M NaOH after 48 hours [34]. Films of poly[bis(trifluoroethoxy)phosphazene] are unaffected by moisture, glacial acetic acid, pyridine, and concentrated caustic solution and high intensity ultraviolet light [35].

Excellent hydrolytic stability has been observed for cyclic poly(organophosphazenes) and for cured elastomeric poly(organophosphazenes). $[(C_6H_5O)_2PN]_3$ trimer underwent no detectable hydrolysis after 200 hours at 100°C in

TABLE I

TRANSITION AND DECOMPOSITION TEMPERATURES FOR
VARIOUS POLY(PHOSHAZENES), $[R_2PN]_n$ [4,27,29]

Polymer R =	(a) T _g , °C	(a) T(1), °C	T _m , °C	(e) T _d , °C
CH ₃ CH ₂ O	-84	--	--	--
CF ₃ CH ₂ O	-65	80	240 (b)	360
C ₆ H ₅ O	5.5	160	390 (b)	380
<u>m</u> -ClC ₆ H ₄ O	-24	66	370 (b)	380
<u>p</u> -ClC ₆ H ₄ O	4	167	365 (c)	410
<u>m</u> -CH ₃ C ₆ H ₄ O	-25	90	348 (c)	350
<u>p</u> -CH ₃ C ₆ H ₄ O	0.3	152	340 (c)	310
<u>p</u> -CH ₃ CH ₂ C ₆ H ₄ O	-18	43	-- (d)	285
<u>m</u> -CF ₃ C ₆ H ₄ O	-35	--	-- (a)(f)	--
			(330)(g)	
<u>p</u> -FC ₆ H ₄ O	-14	--	--	--
<u>β</u> -C ₁₀ H ₇ O	47	--	160 (a)(f)	--
			(>350)(g)	
<u>p</u> -C ₆ H ₅ -C ₆ H ₄ O	43	--	160 & 398 (a)	--
			(>350)(g)	
CF ₃ CF ₂ CF ₂ CH ₂ O [28]	14	--	--	--
CF ₃ (CF ₂) ₆ CH ₂ O	-40	--	--	--
(C ₃ F ₇ CH ₂ O)(CF ₃ CH ₂ O)	-77	--	--	--
C ₆ H ₅ NH	105 (h)	--	--	-- (i)
<u>p</u> -CH ₃ C ₆ H ₄ NH	97 (h)	--	--	250 (i)
<u>m</u> -CH ₃ C ₆ H ₄ NH	76 (h)	--	--	262 (i)
<u>p</u> -C ₂ H ₅ C ₆ H ₄ NH	88 (h)	--	--	245 (i)
<u>m</u> -C ₂ H ₅ C ₆ H ₄ NH	61 (h)	--	--	243 (i)
<u>p</u> -n-BuC ₆ H ₄ NH	53 (h)	--	--	253 (i)
<u>p</u> -CH ₃ OC ₆ H ₄ NH	92 (h)	--	--	266 (i)
<u>p</u> -ClC ₆ H ₄ NH	85 (h)	--	--	265 (i)
<u>m</u> -ClC ₆ H ₄ NH	80 (h)	--	--	253 (i)
<u>p</u> -FC ₆ H ₄ NH	-- (h)	--	--	260 (i)
<u>m</u> -FC ₆ H ₄ NH	80 (h)	--	--	249 (i)

(a) By differential thermal analysis or differential scanning calorimetry.

(b) By optical microscopy and differential scanning calorimetry.

(c) By thermal mechanical analysis.

(d) Decomposes with expansion.

(e) By thermal gravimetric analysis. Results obtained in argon or nitrogen.
Values in oxygen were not significantly different.

(f) The thermogram showed a strongly exothermic reaction above 300°C,
probably degradation taking place which possibly masked the melting
transition above 300°C.

(g) By microscopy.

(h) By duPont 990 thermal analyzer at scan rates of 10°C/min.

(i) By duPont 951 thermogravimetric analyzer at heating rates of 20°C/min.
(static air).

5 volume percent aqueous dioxane with $4.25 \times 10^{-3}N$ NaOH [36]. $[(CF_3CF_2CF_2CH_2O)_2PN]_3$ showed no change after refluxing one hour in 68% HNO_3 [37]. $[(CF_3CH_2O)(C_3F_7CH_2O)PN]_n$, the first elastomeric fluoroalkoxyphosphazene reported, remained unchanged upon prolonged contact with boiling water, common organic solvents, concentrated H_2SO_4 , and concentrated KOH [38].

Excellent hydrolytic stability of compounded poly(fluoroalkoxyphosphazene) interpolymers has been demonstrated. Cured vulcanizates, prepared for elevated service with lubricants and fluids, retain 80% of tensile strength after 888 hours at $100^\circ C$ and 100% relative humidity [39]. Similar vulcanizates, prepared for use as lip seals, show good retention of physical properties after 166 hours at $100^\circ C$ and 100% relative humidity and after 120 hours in 30% KOH at $93^\circ C$ [40a,b].

(c) Thermal Properties

To date the major limitation of poly(organophosphazenes) for use as a matrix resin for advanced composites has been thermal stability. Efforts over the past decade have focused on elastomeric poly(organophosphazenes) for broad temperature serviceability or for highly fire-retardant applications. Consequently, there has been less interest in optimizing the physical and thermal properties of essentially unfilled thermoplastic or thermosetting poly(organophosphazenes).

Isothermal aging of poly(organophosphazenes), neat or in solution, has generally been disappointing. Studies at temperatures of $149^\circ C$ and higher have revealed that crystalline film-forming thermoplastics $[(CF_3CH_2O)_2PN]_n$ [41], $[(C_6H_5O)_2PN]_n$ [42], and $[(m-ClC_6H_4O)_2PN]_n$ [43] and the elastomer $[(CF_3CH_2O)(HCF_2(CF_2)_3CH_2O)(X)PN]_n$ (X = small amount of cross-link site) [44] undergo initial rapid molecular weight degradation followed by a more gradual decrease. Degradation was accelerated in the presence of water or acids. In these studies reaction products were analyzed by gel permeation chromatography and solution viscosity. The degradation mechanism is consistent with an initial random chain scission at weak sites along the polymer, followed by depolymerization to cyclic oligomers [41,42,44]. In the case of $[(m-ClC_6H_4O)_2PN]_n$ no evidence was obtained for depolymerization [43].

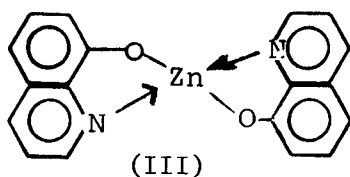
The thermal degradation of poly[bis(p-isopropylphenoxyphosphazene)] was reported very recently [45]. Interestingly, this polymer showed higher thermal stability than other poly(aryloxyphosphazenes) [42,43]. Thermal studies were

conducted in sealed evacuated tubes placed in heated baths. Degradation was followed by gel permeation chromatography. After 1,344 hours at 135°C the \bar{M}_w was 484,000, down from an initial value of 997,800. The lack of formation of cyclic trimeric or tetrameric species suggested degradation exclusively by random scission. After 1,008 hours at 200°C \bar{M}_w was 363,000, with increasing formation of cyclics after 168 hours. Polymer heated at 200°C did not change in physical appearance, although at 300°C the polymer eventually darkened and liquified. Short periods of heating, i.e. 4 hours at 300°C, led to no significant change in Tg or infrared spectrum. As with earlier findings [41-44] the data indicated initial rapid molecular weight reduction followed by a more gradual reduction, both processes seemingly involving scission.

The weak link sites responsible for thermal degradation have been postulated [41,42,44] to include -P-OH, -P(O)-NH(phosphazane), chain branch point, and residual P-Cl sites. Chain scission most likely occurs by attack of a protonic species at a phosphazane site to produce lower molecular weight polymers with active end groups [44].

Several options are available for improving thermal stability of poly(organophosphazenes). These include one or more of the following: (a) provision for effective neutralization of weak links, (b) optimization of the number and type of organic substituents, and (c) removal of weak links.

The approach of deactivating weak sites by the addition of stabilizers was successfully pioneered at The Firestone Tire & Rubber Company [44,46-49]. Specifically, use of 1-3 weight percent bis(8-oxyquinolate)zinc (+2) (III)



has led to greatly improved thermal performance of poly(fluoro-alkoxyphosphazenes) (PFAP). This has been reflected in solution viscosity as well as physico-mechanical properties of vulcanizates as shown in Figures 1 and 2 and Table II. Use of 3 weight percent of bis(8-oxyquinolate)zinc with PFAP affords a molecular weight of 4×10^6 (down from 6×10^6) after 32 hours at 177°C. Without stabilizer the molecular weight drops to 0.3×10^6 under these conditions. The effect of stabilizer also leads to great improvement in properties of O-ring seal formulations after >600 hours aging at 177°-200°C [47].

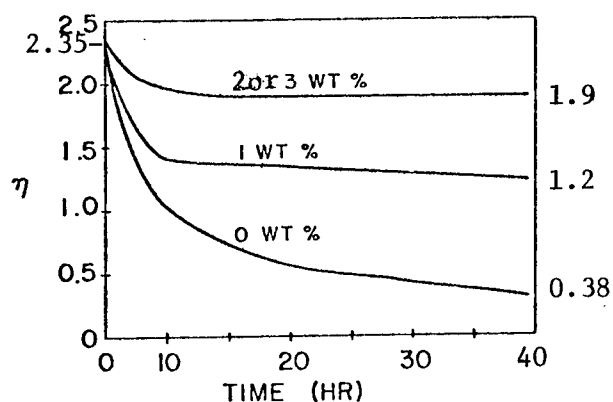


Figure 1

Change in solution viscosity of PFAP [with 0, 1, 2, and 3 wt. % bis(8-oxyquinolate) zinc] with time at 177°C [44].

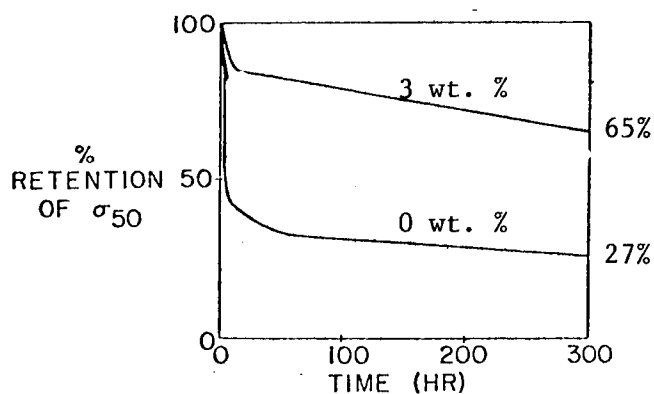


Figure 2

Retention of 50% modulus (σ_{50}) for reinforced PFAP vulcanizates [with 0 and 3 wt. % bis(8-oxyquinolate) zinc] on aging in air at 200°C [44].

TABLE II

EFFECT OF HEAT AGING ON PFAP VULCANIZATE^(a)
PROPERTIES [48]

Stress-Stain Property	Unaged Value	Aged (120 hrs/200°C) Value
50% Modulus, psi	461	317
100% Modulus, psi	1445	937
Tensile strength, psi	1559	1016
Elongation @ break, %	108	110

(a) Contains 2 parts of bis(8-oxyquinolate)zinc.

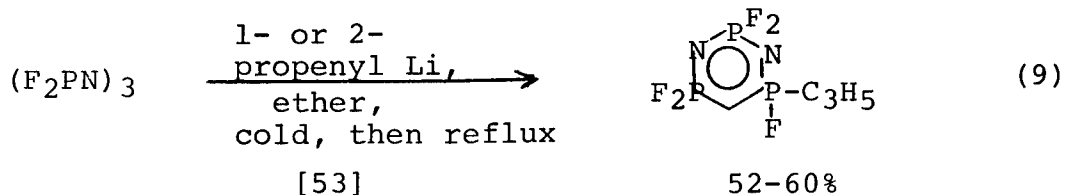
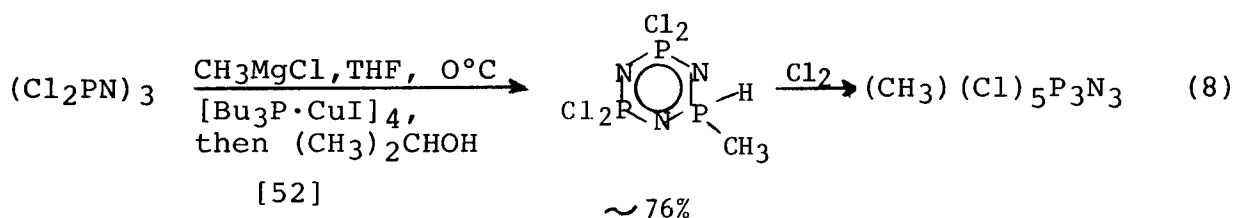
The stability shown by poly[bis(p-isopropylphenoxy-phosphazene)] certainly represents a step forward in the search for more thermally stable poly(organophosphazenes). Another, and more likely approach, to improve thermal stability comprises at least partial replacement of alkoxy or aryloxy substituents bonded to phosphorus by phosphorus-carbon sites, particularly by direct bonding of phenyl or substituted aryl groups to phosphorus. Introduction of significant quantities of P-C

sites in the polymer is anticipated to circumvent the pathways that permit depolymerization or decomposition at $>200^{\circ}\text{C}$. Consequently, higher thermal and photolytic stability will result.

Significant progress has been made in the last two years concerning the preparation of high molecular weight P-carbon containing poly(organophosphazenes) using organometallic reagents (e.g., phenyl lithium or phenyl Grignard) [16,17]. Earlier attempts were unsuccessful primarily due to extensive skeletal degradation [34,50]. Successful phenylation of a high molecular weight $[\text{F}_2\text{PN}]_n$ polymer was described earlier in Section 5.5.2, Equation (3). A high molecular weight $(1.2 \times 10^6) [(\text{O})_{0.62}(\text{CF}_3\text{CH}_2\text{O})_{0.38}\text{PN}]_n$ copolymer was prepared which showed greater resistance to molecular weight decline at 300°C than did the $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}]_n$ homopolymer [16]. TGA results indicated that incorporation of as little as 10 mole % P- ϕ sites raised the decomposition temperature at least 50°C [51].

Unfortunately, the state-of-the-art prevents achievement of high P- ϕ containing poly(phosphazenes) at high molecular weights, i.e., $\geq 5 \times 10^5$. For example, the P-phenyl content could be raised to 84 mole % but molecular weight decreased to about 80,000 [16]. Fully substituted phenylated product could be obtained at a molecular weight of about 2500.

High yields of cyclic phosphazenes with a carbon-phosphorus site have been prepared recently [51,52] as shown in Equations (8) and (9).



The chemistry in Equation (8) is noteworthy because it does not necessitate the use of a poly(difluorophosphazene) intermediate. The phosphine and CuI probably moderate the activity of the organometallic reagent to such an extent that substitution proceeds in high yield without major skeletal degradation. Hopefully this technique may eventually be employed for the preparation of high molecular weight polymer containing carbon-phosphorus bonds.

There are earlier reports in the literature strongly indicative of potential stability of poly(organo-phosphazenes) at temperatures in excess of 300°C. These citations are listed:

1. Hexakis(heptafluorobutoxy)cyclotriphosphazene, $[(C_3F_7CH_2O)_2PN]_3$, gave 50% of the corresponding tetramer after 50 hours of heating at 340°C [37].
2. Diphenylcyclophosphazenes (presumably tri- and tetramer) did not thermally rearrange but at 400°C benzene elimination began [34]. This does not preclude the possibility of extended service at 350°C. Cyclic trimer melts at 226-227°C [22].
3. Hexakis(3- or 4-trifluoromethylphenoxy)cyclotriphosphazene remained unchanged after heating at 410°C (770°F) for 10 hours [54].
4. Hexakis(phenoxy)cyclotriphosphazene is used as a high temperature standard for mass spectrometry [55].
5. Poly[bis (trifluoromethyl)phosphazene], $[(CF_3)_2-PN]_n$ showed a decomposition or depolymerization temperature near 380°C [33].
6. $\dagger NC_3N_3(\emptyset)-N=P(\emptyset)_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-P(\emptyset)_2\dagger_{12}$ lost 6% of its weight in air up to 420°C (TGA) and several other compositions showed no weight loss up to 390°C (TGA, air) [24].

(d) Physico-Mechanical Properties

Although there have been a number of reports describing physico-mechanical properties of filled cured poly(organo-phosphazene) elastomers, little information is available concerning these properties of poly(organo-phosphazene) thermoplastics. Most of these thermoplastics orient upon

drawing and in so doing show a substantial increase in tensile strength and a substantial decrease in elongation as shown in Table III. Properties of $[(p\text{-ClC}_6\text{H}_4\text{O})_2\text{PN}]_n$ film (similar in appearance to polyethylene) which had been cast into clear thin films ($8\text{-}10 \times 10^{-3}$ nm thick) are shown in Table IV.

TABLE III

TENSILE PROPERTIES OF POLY(FLUOROALKOXYPHOSHAZENE)
CAST FILMS [56]

	Unoriented (10-15 mils)	Oriented (3-5 mils)
$[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}]_n$		
Yield strength (psi)	1,220	--
Tensile strength at break (psi)	1,250	7,690
Elongation (%)	130	50
Tensile modulus (psi)	162,500	384,500
$[(\text{C}_3\text{F}_7\text{CH}_2\text{O})_2\text{PN}]_n$		
Yield strength (psi)	430	--
Tensile strength at break (psi)	750	6,800
Elongation (%)	785	60
Tensile modulus (psi)	553,425	408,000

TABLE IV

TENSILE TEST OF POLY[DI(p-CHLOROPHENOXY)PHOSHAZENE]
FILMS [27]

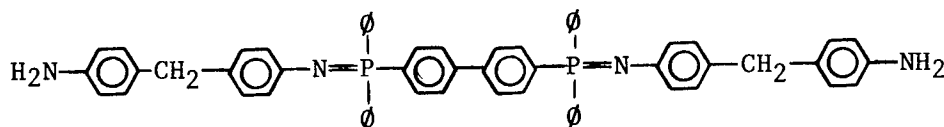
Sample ^a	Untreated Film	After 48 hrs in water at 25°C	After 8 hrs in water at 100°C
Initial modulus (kg/cm ²)	4,700	3,900	3,400
Yield stress (kg/cm ²)	210	220	180
Elongation (%)	100	83	108

^aFor comparative purposes initial moduli (kg/cm²) of polyethylene and polypropylene are 10^3 and 10^4 , respectively.

(e) Phosphazene Composites

Little information exists concerning the use of poly(phosphazenes) for fabrication of composites. Several $[(CF_3CH_2O)_x(NH_2)_yPN]_n$ copolymers were synthesized from relatively low molecular weight $[Cl_2PN]_{n=40-80}$ polymer for evaluation as possible laminating resins [57]. These resins were evaluated with silica cloth but none gave high tensile strengths and all decomposed above $300^\circ C$. However, thermally crosslinked products obtained by partial amination of $(Cl_2PN)_3$ gave hydrolytic and thermal stabilities comparable to aryloxy- and aryl-substituted poly(phosphazenes). Heating above $500^\circ C$ eventually led to formation of phosphorus nitride.

Recently, low molecular weight amine terminated arylated poly(phosphazene) was used to prepare a flame retardant modified polyimide for composite fabrication [24]. Feasibility of the PMR (Polymerization of Monomer Reactants) technique to prepare glass laminates was established. The organic components for the PMR system comprised 4,4'-methylenedianiline, monomethyl ester of norbornene-2,3-dicarboxylic ester, dimethyl ester of 3,3',4,4'-benzophenone tetracarboxylic acid with or without the phenylated poly(phosphazene) (IV).



(IV)

The phosphazene modified product showed high thermal stability, no weight loss to $390^\circ C$, and a char yield of 47% at $600^\circ C$. Properties of the phosphazene modified polyimide glass laminates are compared to polyimide system in Table V. Clearly the phosphazene modified materials were inferior to the wholly polyimide materials.

Asbestos (Chrysotile) reinforced composites were prepared [58] from poly(decaboranyl-phosphazenes) of structure (V) [59].

TABLE V

MECHANICAL PROPERTIES OF PMR POLYIMIDE AND POLYPHOSPHAZENE-POLYIMIDE/-
GLASS LAMINATES [24]

Laminate No. a	% Resin Content	Flexural Strength $N/m^2 \times 10^{-6} (\text{psi} \times 10^{-3})$			Interlaminar Shear Strength $N/m^2 \times 10^{-6} (\text{psi} \times 10^{-3})$			
		RT ^b	204°C (400°F)	316°C (600°F)	RT	204°C (400°F)	316°C (600°F)	
3	33	362 (52.5)	265 (38.4)	226 (32.8)	46 (6.60)	32 (4.60)	22 (3.15)	
4	34	360 (53.4)	311 (45.0)	317 (46.0)	35 (5.00)	35 (5.10)	32 (4.65)	
5	37	366 (53.1)	328 (47.6)	338 (49.0)	53 (7.70)	37 (5.43)	31 (4.50)	
8	32	207 (30.0)	104 (15.0)TP ^c	83 (12.0)TP	20 (4.06)	F ^d	F	
9	24 ^e	207 (30.0)	104 (15.0)	55 (8.0)	19 (2.70)	F	F	
10	27 ^e	207 (30.0)	90 (13.0)	52 (7.6)	18 (2.67)	F	F	

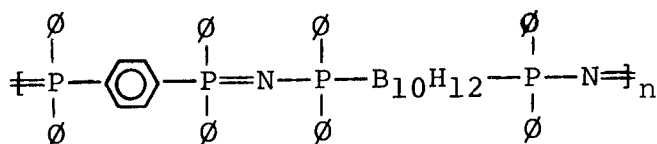
a) Samples 8-10 contain poly(phosphazene) (IV)

b) Room temperature

c) Thermoplastic (TP)

d) Thermoplastic failure (F)

e) Excessive resin flow during molding



(V)

Polymer (V) starts to soften above 340°C accompanied by the release of hydrogen. Results of isothermal aging in air of (V) at two molecular weights is shown in Table VI, and the effects of composite aging on flexural strength and modulus is shown in Figures 3 and 4. Composites derived from

TABLE VI
ISOTHERMAL HEAT AGING IN AIR
OF POLY(DECABORANYL-PHOSPHAZENES) [58]

% Weight loss After Cumulative Exposure

Resin (%)	Aging Temperature °F		
	700 (371°C)	800 (427°C)	900 (482°C)
PNP-II(a)	4.9/48 hrs.	8.5/29 hrs.	13.1/24 hrs.
PNP-III(b)	1.0/6 "	1.6/8 "	2.4/3 "

(a) Molecular weight in excess of 20,000.

(b) Oligomeric; readily soluble in a number of solvents.

polymer (V) have several limitations; the resin shows limited solubility, composite fabrication requires relatively severe processing conditions, the resin is hydrolytically unstable, and the resin evolves hydrogen starting at about 270°C.

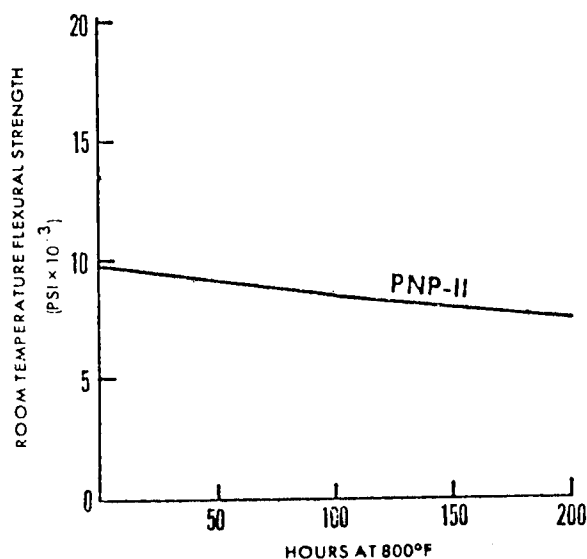


Figure 3

Effect of Heat Aging on Flexural Strength of Poly(decaboranyl-phosphazene) Composites [58].

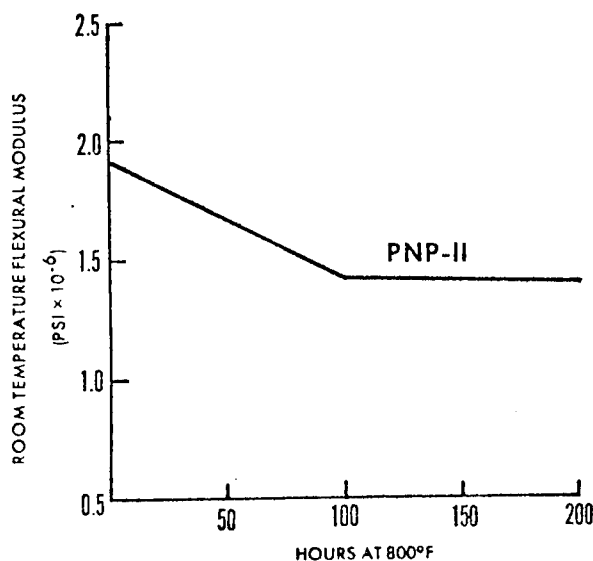


Figure 4

Effect of Heat Aging on Flexural Modulus of Poly(decaboranyl-phosphazene) Composites [58].

(f) Crosslinking

Physico-mechanical properties as well as thermo-oxidative behavior is invariably improved by proper polymer crosslinking. For example, introduction of vinyl functionality with subsequent cure of a poly(silarylene-siloxane) significantly improved thermal stability [60] (also see Section 5.2.3).

Numerous examples of crosslinking poly(organo-phosphazene) elastomers have been cited [1,8-10,12,39,40,44,46-49,61-63]. Crosslinking was generally achieved by use of an organic peroxide or a sulfur accelerated system at temperatures of 140°C to 175°C. Increased versatility of cure site structure and method(s) for its introduction into a poly(organo-phosphazene) should further advance the development of improved phosphazene materials. To a large extent this has been accomplished [64] by modifying the substitution reaction of $[\text{Cl}_2\text{PN}]_n$ polymer (see Equation 2). Replacement of the conventional sodium alkoxide nucleophile by an organic hydroxyl reactant in the presence of triethylamine allows for the introduction

of a number of different cure sites, many of which can be activated at low temperatures.

Another method of crosslinking poly(organophosphazenes), not dependent on an unsaturated cure site, was accomplished by ligand exchange on poly(fluoroalkoxyphosphazenes) [65a,b]. $[(CF_3CH_2O)_2PN]_n$ and $[(CF_3CF_2CF_2CH_2O)_2PN]_n$ were crosslinked at 25°C in tetrahydrofuran or Freon TA solvent by reaction with the disodium salt of 2,2,3,3,4,4-hexafluoropentenediol.

(g) Miscellaneous Properties

1. Fiber formation:

Several poly(organophosphazenes) can be fabricated into fibers. Elastic fibers of $[(CF_3CH_2O)_2PN]_n$ were prepared by extrusion of polymer into a nonsolvent [35]. Poly[bis (p-phenylphenoxy)phosphazene], $[(p-C_6H_5C_6H_4O)_2PN]_2$, formed fibers quite readily from the melt at 225°C [27]. Undrawn monofilaments of diameter 50-60 μm gave a Young's Modulus of 2.14×10^{10} dyn/cm² (2.14×10^9 N/m²) which is about the same as undrawn nylon.

2. Radiation resistance:

Exposure of $[(CH_3)_2PN]_n$ to 40 Mrads (Co⁶⁰ source) at 150°C decreased the molecular weight from 11,000-12,000 to 6,000-7,000 and broadened the melting point from 139-142°C to 137-145°C [26]. In addition, PNF[®] shows good resistance to radiation, ozone, and N₂O₄ [40].

(h) Economic

Polymerization of (Cl₂PN)₃ trimer is the recommended route to the preparation of high molecular weight poly(organophosphazenes). The trimer is prepared from PCl₅ and NH₄Cl which in turn are prepared from the appropriate combinations of P, Cl₂, NH₃, and HCl. In volume it is likely that

the trimer would be expected to sell for \$3-\$5/lb. Polymerizations are usually carried to 30-50% conversion. Monomer and solvent (if employed) would be readily recovered and therefore no significant additional increase in materials cost is anticipated. Commonly employed phenols used for the preparation of poly(aryloxyphosphazenes) (APN) are generally priced in the range \$0.25-\$1.00/lb. Therefore the price of APN should be in the range of \$5-\$10/lb.

High P-phenyl containing poly(organophosphazenes) derived from a poly(dichlorophosphazene) intermediate would cost more, at least 25%, than APN materials because of the organometallic reagents (e.g., ØLi , ØMgBr) employed.

Preparation of high P-phenyl containing polymers via poly(difluorophosphazene) intermediate as shown in Equation (3) would greatly increase the cost of poly(organophosphazene). This is anticipated because of costlier halogenated intermediates, more expensive equipment, and more expensive solvents (see Section 5.5.2).

Introduction of a simple cure site derived from readily available intermediates should not significantly effect the price structure. Costly reagents (\$5-\$10/lb) would only marginally increase the cost (ca. 50¢/lb) of the final polymer because they would be employed in small amounts (1-5%).

5.5.4 Summary and Recommendations

Poly(organophosphazenes) have been extensively studied and offer unique advantages as potential matrix resins for advanced composites;

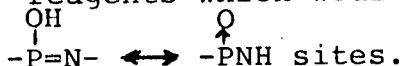
- (a) Ability to be prepared in very high molecular weight from relatively simple materials [i.e., $(\text{Cl}_2\text{PN})_3$, alcohols, phenols],
- (b) Virtually unlimited structure-property control, and
- (c) Ease of introduction of cure site.

The major obstacle to development is limited thermal stability, although major strides have been made in recent years by way of structure improvement and deactivation of weak links. This positive trend is expected to continue with future efforts focusing upon:

- (a) Polymerization of $[(Cl_{6-x}(\emptyset)_xPN)]_3$ ($x = 1, 2$) and its copolymerization with $(Cl_2PN)_3$ to afford high molecular weight polymers containing 10-15 mol % P-phenyl sites. The remainder of organic substituents bonded to phosphorus would be selected from aryloxy groups because these structures appear to offer the best combination of thermal stability, high transition temperatures, and processability. The above level of P-phenyl might be sufficient to significantly block thermal degradation by a depolymerization mode at temperatures of ca. 300°C. This blocking approach* has a successful parallel in poly(siloxane) chemistry, and also might be the explanation for the improved thermal stability of poly(organophosphazenes) resulting from treatment with a lithium carborane-containing phenolate or alcoholate [66].

It is unknown at this time as to whether high ($\geq 75\%$ mol) P-phenyl containing poly(organophosphazenes) would be thermally superior to the best known poly(organophosphazenes). The question* as to whether intramolecular steric hindrance in polymer relative to that in cyclic oligomers would act as a thermodynamic driving force for depolymerization [1,41], in the absence of "weak links", is yet to be answered.

- (b) Reduction of the number of weak links in poly(organophosphazenes). Two approaches can be visualized. First, attempt the purification, polymerization of $(Cl_2PN)_3$, and its quantitative conversion (final % Cl as P-Cl $\leq 0.01\%$) to poly(organophosphazene) under scrupulously dry conditions. Second, identification of new reagents which would react irreversibly with



- (c) Design of a volatile-free crosslinking system which would permit processability under modest temperature-pressure conditions. Crosslinking by a ligand exchange [see Section 5.5.3(f)] reaction of metal salts might be advantageous. Variation in crosslinker structure should afford wide latitude in cure temperature and time under conditions where no volatiles are formed. It would also be worthwhile to study the effect of solid poly(nucleophilic) specie upon

*Also see Section 4.1.2a.

conventional poly(aryloxyphosphazenes). Aryloxide nucleophiles would be most suitable at elevated temperatures since salts of polyfluorinated alcohols are thermally unstable.

5.5.5 Bibliography

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Allcock, H. R., Dept. of Chemistry, Pennsylvania State Univ., University Park, PA 16802.

Bailar, Jr., J. C., Dept. of Chemistry, University of Illinois, Urbana, IL 61801.

Block, B. P., Pennwalt Corp., King of Prussia, PA 19406.

Carraher Jr., C. E., Dept. of Chemistry, Wright State Univ., Dayton, OH 45431.

Frye, C. L., Dow-Corning Corp., Midland, MI 48640.

Griffith, J. R., Naval Research Lab., Chemistry Section, Washington, DC 20375.

Lenz, R. W., Chemical Engineering Dept., University of Massachusetts, Amherst, MA 01002.

Neuse, E. W., Dept. of Chemistry, University of the Witwatersrand, Johannesburg, South Africa.

Peters, E. N., Union Carbide Corp., Tarrytown, NY 10591.

Pittman Jr., C. U., Dept. of Chemistry, University of Alabama, University, AL 35486.

Rosenberg, H., AFML, Wright Patterson Air Force Base, Dayton, OH 45433.

Sheats, J. E., Dept. of Chemistry, Rider College, Lawrenceville, NJ 08648.

Singler, R. E., Organic Materials Lab., Army Materials & Mechanics Research Center, Watertown, MA 02172.

Stewart, D. D., Union Carbide Corp., Bound Brook, NJ 08805.

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Tate, D. P., Central Research Laboratories, The
Firestone Tire & Rubber Co., Akron, OH
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